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Single Laboratory Validation of EPA (Environmental Protection Agency) Method 8030 Acrolein, Acrylonitrile, and Acetonitrile

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16. ABSTRACT

USEPA Method 8030 was modified and evaluated with revised chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile in groundwater, solid, and organic liquid matrices. Groundwater was analyzed by the heated purge-and-trap method; a solid waste was analyzed by the polyethylene glycol (PEG) heated purge-and-trap technique and by the heated headspace method; and a liquid organic waste was analyzed by direct liquid injection and by the heated headspace method.

The heated purge-and-trap method gave excellent recoveries (85 to 96%) and precision for the three analytes in groundwater. The PEG/heated purge-and-trap method gave good recoveries (76 to 96%) for acetronitrile and acrylonitrile in the solid waste but poor recoveries for acrolein (10%). Problems encountered from the carry-over of PEG indicated that additional modifications of this method are needed. The direct liquid injection technique gave excellent results for the determination of all three analytes (86 to 111% recoveries) in the organic liquid waste. The manual heated headspace method gave distinctly less accurate and less precise results than the PEG/purge-and-trap method for the determination of acetonitrile and acrylonitrile in the solid waste sample. Acrolein was not recovered at all by the method. The headspace method gave extremely erratic results for the analysis of the organic liquid waste.

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SINGLE LABORATORY VALIDATION OF EPA METHOD 8030 -- ACROLEIN, ACRYLONITRILE, AND ACETONITRILE

by

Samuel V. Lucas, Thomas F. Cole,
Alice Riggin, and W. Marcus Cooke

BATTELLE
Columbus Laboratories
Columbus, Ohio 43201-2693

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James E. Longbottom
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory, Cincinnati, Ohio conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report presents the results of the evaluation of Method 8030 for the analysis of acrolein, acrylonitrile, and acetonitrile using improved chromatographic conditions and also presents the results of evaluations of three different sample introduction techniques for the analysis of these substances in a variety of matrices of environmental interest.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory-Cincinnati

ABSTRACT

EPA Method 8030 was modified and evaluated with revised chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile, in groundwater, solid, and organic liquid matrices. Method validation studies were conducted on each of the four sample preparation techniques included in Method 8030, namely (1) heated purge-and-trap; (2) polyethylene glycol (PEG) extraction followed by heated purge-and-trap; (3) direct liquid injection; and (4) manual heated headspace. Each method validation involved the determination of the method detection limit (MDL) and seven replicate analyses of one or two matrices unspiked and spiked at two different levels. Groundwater was analyzed by the heated purge-and-trap method; a solid waste was analyzed by the PEG/heated purge-and-trap technique and by the heated headspace method; and a liquid organic waste was analyzed by direct liquid injection and by the heated headspace method.

The heated purge-and-trap method gave excellent recoveries (85 to 96 percent) and precision for the three analytes in groundwater. The PEG/heated purge-and-trap method gave good recoveries (76 to 96 percent) for acetonitrile and acrylonitrile in the solid waste but poor recoveries for acrolein (10 percent). Problems encountered from the carryover of PEG indicated that additional modifications of this method are needed. The direct liquid injection technique gave excellent results for the determination of all three analytes (86 to 111 percent recoveries) in the organic liquid waste; however, late eluting material may present serious problems in some cases. The manual heated headspace method gave distinctly less accurate and less precise results than the PEG/purge-and-trap method for the determination of acetonitrile and acrylonitrile in the solid waste sample. Acrolein was not recovered at all by the method due, apparently, to decomposition during the one-hour equilibration at 90°C. The headspace method gave extremely erratic results for the analysis of the organic liquid waste and was, therefore, considered completely unsatisfactory for such samples.

This report was submitted in partial fulfillment of Contract Number 68-03-1760, Work Assignment Number 3, by Battelle's Columbus Laboratories. The research reported here was conducted under the sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1

INTRODUCTION

The objective of this program was to perform single-laboratory validation of U.S. EPA/OSW Method 8030, which covers the gas chromatographic (GC) determination of acrolein, acrylonitrile, and acetonitrile in groundwater and liquid and solid wastes.

Method 8030 (Appendix A) provides four sample preparation options: (1) heated purge-and-trap (HP&T) using EPA Method 5030; (2) polyethylene glycol extraction followed by heated purge-and-trap (PEG/HP&T) using EPA Method 5030; (3) direct liquid injection onto the GC column (DLI); and (4) heated headspace sampling (HHS) using EPA Method 5020.

This method validation study was undertaken in response to a variety of prior experience which suggested that Method 603, on which Method 8030 is based, was not a reliable analysis method. For example, a previous single laboratory method validation study performed for EPA by another contracting laboratory produced no useful data. In addition, several investigators have querried EPA regarding difficulties with the reproducibility of the gas chromatography and problems encountered from acetone interference. Thus, development and use of improved chromatographic conditions was a critical first step in this work.

Table 1 indicates the scope of this method validation study by showing the seven replicate data sets which are reported here. In addition, the linear dynamic range of the GC flame ionization detector (FID) was also evaluated for the three method analytes.

TABLE 1. SCOPE OF THE METHOD VALIDATION EXPERIMENTS PERFORMED

Method (Matrix)	Seven Replicate Data Set Obtained (x)			
	MDL[a]	Nonspike	Low Spike[b]	High Spike[b]
5030, HP&T (groundwater)	(c)	(d)	X	X
5030, PEG/HP&T (solid waste)	X	(d)	X	X
DLI (liquid waste)	X	X	X	X
5020, HHS	X			
(liquid waste)		X	X	X
(solid waste)		X	X	X

(a) The matrix for method detection limit (MDL) was reagent water for all but DLI for which the matrix was toluene.

(b) Low spike levels were chosen to be at or near the MDL level when possible; high spike levels were generally 10-fold higher.

(c) The groundwater low spike data were used to compute MDL.

(d) Three to six replicates of unspiked samples were analyzed with both the low and high spike data sets; no separate seven replicate experiment was performed.

SECTION 2

CONCLUSIONS

The validation results contained in this report support the following conclusions regarding the performance of Method 8030 and associated sample introduction techniques for the determination of acetonitrile, acrolein, and acrylonitrile in groundwater, a solid waste, and an organic liquid waste:

- The previously recommended GC column (Chromosorb 101) is unsuitable for the separation of acetonitrile from acrolein and acrolein from acetone, a common interference.
- The heated purge-and-trap analysis option (Method 5030) works very well for the determination of low parts-per-billion levels of the method parameters in groundwater.
- The polyethylene glycol (PEG) sample preparation method for solids (Method 5030) provides good precision and accuracy at the low parts-per-million level, but is subject to failure upon extended use due to apparent aerosolization of PEG which contaminates the purge-and-trap apparatus and leads to inconsistent results.
- The PEG cleanup procedure from Method 5030 is not extensive enough to provide sufficiently clean reagent to analyze for the method parameters at low parts-per-million levels.
- Acrolein stability is not understood completely, and more work is necessary to develop sample preservation criteria for this analyte particularly in solid matrices.
- The direct organic liquid sample introduction technique is precise and accurate for the determination of method parameters at low parts-per-million levels.
- The manual heated headspace procedure does not provide acceptable results for analysis of the organic liquid waste sample and provides such a high level of imprecision for solid samples that it should be used only for approximation (i.e., a maximum of one significant figure).

- The manual heated headspace procedure provides a reliable estimate of levels of the method parameters in an aqueous matrix at levels above one part-per-million, but the method is useful only for an initial screening of such samples since purge-and-trap analysis is the method of choice for aqueous samples.

SECTION 3

RECOMMENDATIONS

Based upon the results of the evaluations conducted under this research program, the following recommendations are made:

- The method should be revised to include Porapak QS as the primary GC column packing material. Chromosorb 101 should be recommended as the alternate column packing only for those applications for which it is known that either acrolein or acetonitrile is absent and that acetone interference is not expected.
- Further evaluation of the conditions which affect the stability of acrolein should be conducted.
- An improved PEG cleanup procedure is necessary for Method 5030 in order to achieve low parts-per-million detection limits.
- Improvements to the PEG/purge-and-trap procedure should be investigated in order to eliminate carryover of PEG into the purge-and-trap apparatus.
- Method 5020 should be used only for screening of samples or for order-of-magnitude estimation of analyte levels. Whenever the matrix is sufficiently free from interference, organic liquids are best analyzed using the direct liquid injection technique. Similarly, solid samples will give more reliable results when analyzed by the PEG/purge-and-trap procedure of Method 5030 as was found in this study.

SECTION 4

EXPERIMENTAL PROCEDURES

APPARATUS

The following equipment was employed in this research program.

Gas Chromatograph:	Varian 1400; FID detector Varian 3700; FID detector
Purge-and-Trap Apparatus:	Tekmar Model LSC-2
Purge Vessel:	Standard 5-mL vessel with glass frit bottom as provided by Tekmar (No. 14-0042-024) or Supelco (No. 2-2424)
Heated Purge Bath:	1-liter beaker containing 0.9 liter water and a 2-inch magnetic Teflon-coated stirbar. A stirring hot plate controlled by a Variac was used to maintain 85 ± 2°C. The temperature was monitored by a calibrated digital thermometer
GC-Tekmar Interface:	The Tekmar heated transfer line was connected to the packed column injector inlet so that the usual syringe/septum injections could be performed without disturbing the Tekmar connections. There were no unheated transfer line sections
Heated Headspace Equilibration Bath:	Precision Scientific Model 66552/188; maintained at 90 ± 1°C
Headspace Injection Syringe:	Glenco No. K260-250-2200 with 22 ga. 2 inch x 0.016 inch ID needle; without valve
Purge-and-Trap Sample Handling Syringe:	Glenco No. K260-250-2200 with valve and Luer fitting

Rotary Evaporation:	Buchi "Rotovapor-RE" with Welch 1402 vacuum pump and McLeod vacuum gauge
Chromatography Data System:	All validation data were processed using a Computer Inquiry Systems, Inc., (CIS) Computer Automated Laboratory System (CALS) operated on an HP-1000 minicomputer. All signal intensity/time data were archived on 9-track tape

REAGENTS

The following are the reagents and chemical supplies that were used in this work.

Reagent Water:	Reagent water was prepared by passing boiled water from a Milli-RO/Milli-Q system through a column (40 cm x 2.8 cm ID) containing granular activated carbon with integral 300 mL reservoir. The column reservoir was protected from laboratory air with a drying tube filled with the same activated carbon
Granular Activated Carbon:	Barneby and Cheney Type PC, Lot 2547
Acetonitrile:	Burdick and Jackson, No. 15 (UV grade), Lot AJ543
Acrolein:	Aldrich No. 23,954-2, 99+%, Lots 2511JK and 1311TE
Acrylonitrile:	Aldrich No. 11,021-3, 99+%, Lot 2020HK
1-Chloropropane:	Aldrich No. C6,855-5, 99% Lot 7718LH
Polyethylene Glycol (PEG):	Aldrich No. 20,239-8, Average MW 400, Lot 0218BK
Toluene:	Burdick and Jackson, "Distilled in Glass," Lot A1314
Sodium Citrate:	J. T. Baker, "AR", Trisodium Citrate Dihydrate, crystalline

Citrate Buffer Preparation: A 0.1 M stock solution of pH 4.5 citrate buffer was prepared by adding 5.9 g sodium citrate to 200 mL of reagent water and adjusting to pH 4.5 with 9 M sulfuric acid using a pH meter. The buffer was then placed in a clean 500-mL glass bottle and purged overnight with helium at a flow rate of approximately 20 cc/min prior to storage

Standard pH 4.00 Buffer: Fisher "Certified" No. SO-B-98 Lot 734836-24; Potassium Biphthalate, 0.05 M.

METHOD MODIFICATIONS

Three modifications to Method 8030 were made prior to the initiation of the method validation studies:

- Use of a different GC column and GC conditions
- Use of different trap desorption and bake-out conditions
- Improvement of the method for making stock solutions from neat reagents.

All other procedures specified in EPA Method 8030 were observed for the method validation work. There were no modifications to Method 5020 (heated headspace). The only modification of Method 5030 (PEG mediated purge-and-trap) concerned the cleanup procedure required by the PEG used in this work. Methods 8030, 5020, and 5030, as provided by EPA, appear in Appendices A through C, respectively. The modified procedures and analysis conditions are described below.

Gas Chromatographic Analysis Conditions

Column: 10 ft x 2 mm ID, glass; packed with Porapak QS, 80/100 mesh

Carrier Gas: Helium at 30 ± 3 mL/min

Temperature Programs:	
• Purge-and-Trap (including PEG extracts)	110°C, 1.5 min (during trap desorption); ballistically to 150°C; isothermal at 150°C for 18 min; ballistically to 190°C for 10 min
• Direct Liquid Injection and Heated Headspace	150°C isothermal for 12 min; ballistically to 230°C and hold for 35 min (DLI) or 17 min (HHS)
Zone Temperatures:	Injector and detector, 200°C

Trap Desorption and Bake-out Conditions

For both direct purge-and-trap and PEG extract purge-and-trap, the adsorption trap was desorbed at 180°C for 1.5 min. The 1.5 min desorption time began when the trap heater achieved 50°C, and 180°C was achieved on the trap outside surface within 20 sec of that time. The trap bake conditions were 210°C for 10 min at the same flow rate (20 mL/min) as that used for sample purging.

Preparation of Standards

All calibration standards were prepared from 2.00 mg/mL aqueous stock solutions which were prepared from neat reagents. The neat reagents (20.0 mg) were measured volumetrically using 25 or 50 µL syringes (Hamilton Company, Reno, Nevada) into reagent water in a 10-mL volumetric flask which had been underfilled by the amount of neat reagent to be added (25.5 µL, 23.7 µL, and 24.8 µL for acetonitrile, acrolein, and acrylonitrile, respectively). The syringes used were gravimetrically calibrated (± 0.2 mg) to the volume required to deliver 20.0 mg, and they were used only for the preparation of standards throughout the entire study. The neat reagent was added to the water with the flask in a horizontal position so added reagent could not rise to the water/air interface. The flask was then stoppered and shaken thoroughly before returning to an upright position to prevent loss of volatile reagent to the air. Immediately after preparation, the stock solutions were bottled headspace-free in 1.8-mL screw cap vials with Teflon-faced septa seals and stored on ice or at 4°C until use. Each day that analyses were performed, the acrolein stock solution was prepared from neat reagent immediately prior to use. Generally, acetonitrile and acrylonitrile aqueous stocks were used within three to five days after their preparation from neat reagent.

PEG Cleanup Procedure

Method 5030 specified that commercial PEG of nominal molecular weight 400 should be cleaned of potential volatile interferants using heated (90-100°C) rotary evaporation under a pressure of 10 mm Hg or less for at least one hour. The first 500-g batch of PEG was cleaned for 17 h according to these instructions using the apparatus listed above. A mercury-filled McLeod gauge indicated that the vacuum was 0.8 to 1.5 torr throughout the cleanup period. Since the product PEG was still not adequately clean in the GC elution range of the method parameters, the PEG was further cleaned by He purging at 60 mL/min overnight at 190°C. Preparation of the second batch of PEG employed a 72-h 90°C rotary evaporation treatment as before except that N_2 was slowly bubbled through the rotating sample to remove volatile material more quickly. The N_2 flow resulted in a total pressure ranging from 1.5 to 3.0 torr. Nevertheless, this batch also required overnight helium purging at 190°C, as above. The third batch was processed exactly as the second batch except that the total time of rotary evaporation was 20 h.

LINEAR DYNAMIC RANGE OF THE DETECTOR

The linear dynamic range (LDR) of the gas chromatographic system was determined for acetonitrile, acrolein and acrylonitrile using the same GC conditions as those for direct liquid injection described above. Aqueous standards for direct injection were prepared the day of use from individual 2 mg/mL aqueous stock solutions described above using syringes and 10-mL volumetric flasks. Reagent water, Milli-RO/Milli-Q, was used without buffering or pH modification. The standards were bottled headspace-free in 1.8 mL vials with Teflon-lined septa seals and stored on ice during use. Each vial was sampled through the septum only once or twice to avoid headspace accumulation. Due to the number of analyses required to span the range of interest, the low end and high end of the tested dynamic range were generated on separate days. The first day concentrations were 0.0, 0.5, 1.0, 2.0, 4.0, 15.0, and 50 µg/mL. On the second day, the levels were 0.0, 4.0, 15.0, 50, 100, 250, and 500 µg/mL. The 4.0, 15.0 and 50 µg/mL samples were analyzed in quadruplicate each day while all others were analyzed in triplicate. Each standard contained 1-chloropropane internal standard at the 15 µg/mL level. All injections were 2.0 µL, and the analysis order was random.

VALIDATION OF THE AQUEOUS PURGE-AND-TRAP METHOD

Sample Acquisition and Storage

Groundwater was obtained from the well of a Battelle staff member who lives in rural Union County, Ohio. The well depth was approximately 30 ft, and the raw groundwater can be broadly classified as very hard with high levels of carbonate and iron. Two 1-gallon glass jugs with Teflon-lined screw caps were filled headspace-free with freshly pumped groundwater and transported directly to the laboratory. One 1-gallon sample was used on the day of sampling to prepare the high spike level samples. The remaining 1-gallon sample was stored on ice until use on the following day to prepare the low spike level samples.

Preparation of Spiked Groundwater Samples

High Spike Level--

Groundwater was buffered by the addition of 10 mL of 0.1 M pH 4.5 citrate buffer to each of two 1-L volumetric flasks. One flask was mixed and transferred to 40-mL screw cap volatile organic analysis (VOA) vials headspace-free and sealed with Teflon-lined silicone septa. The VOA vials and seals had been prepared by thorough washing and were stored at 110°C until just prior to use. The second flask was spiked with acetonitrile at the 150 µg/L level, 75 µL of 2.00 mg/mL aqueous stock, and with acrolein and acrylonitrile at the 75 µg/L level, 37.5 µL each of individual 2.00 mg/mL aqueous stocks. After dilution to volume and mixing, the VOA vials were immediately filled, as above; both spiked and unspiked samples were stored inverted on ice until analysis on the following day.

Low Spike Level--

Groundwater was buffered and unspiked samples were prepared as described above for the high spike level samples. The second 1-liter flask was spiked with acetonitrile at the 10.0 µg/L level using 5.00 µL of 2.00 mg/mL aqueous stock, acrolein at the 5.0 µg/L level using 2.50 µL of 2.00 mg/mL aqueous stock, and acrylonitrile at the 10.0 µg/L level using 5.00 µL of 2.00 mg/mL aqueous stock. After mixing, 40-mL VOA vial samples were filled as described above and stored inverted on ice overnight prior to analysis.

Preparation of Calibration Standards

A 10-fold calibration concentration range for each analyte was established on each day of purge-and-trap analysis. The calibration ranges used on a given day encompassed the corresponding spiking level for the respective analytes. Calibration standards were always prepared from previously unused 1.8-mL vials of 2.00 mg/mL aqueous stock. Calibration standards containing all three analytes were prepared on the day of use from the 2.00 mg/mL aqueous stock solutions using microliter syringes and 10-mL volumetric flasks. The water used for preparing standards was boiled Milli-RO/Milli-Q reagent water. Immediately after preparation, such calibration standards were bottled headspace-free and kept on ice until use. Purged calibration standards spanning the 100-fold calibration range (see chart below) were prepared by adding the appropriate amounts of spiking concentrate to 5.0 mL of reagent water in the 5-mL sample transfer syringe. Vials of calibration spiking stock were discarded when their use had resulted in 100 L or more of headspace in the vial.

Calibration Standard Level, μg/L(a)	Concentration of Spiking Stock, mg/L(a)	Volume of Spiking Stock Used for 5.0 mL Water
2/1/1	1/0.5/0.5	10 μL
6/3/3	1/0.5/0.5	30 μL
20/10/10	10/5/5	10 μL
60/30/30	10/5/5	30 μL
200/100/100	10/5/5	100 μL

(a) Analytes are listed in the following order: acetonitrile/acrolein/acrylonitrile.

Use of 1-Chloropropane Internal Standard

Stock solutions of 1-chloropropane internal standard (IS) at 30 mg/mL were prepared in methanol by adding 337 μL via a 500 μL syringe of 1-chloropropane to 8 mL of methanol in a 10-mL volumetric flask followed by dilution to 10.0 mL and mixing. The methanol stock was immediately bottled headspace-free for later use as described above. An aqueous spiking solution of the internal standard was prepared each day just prior to use by adding 5.0 μL of the 30 mg/mL IS methanol stock to 5.0 mL of boiled, headspace-free reagent water in a 5-mL gas tight syringe fitted with a valve. The syringe contained a Teflon O-ring for mixing the headspace-free standard. This aqueous internal standard spiking solution (30 μg/mL) was kept on ice through the day. Each 5-mL sample or calibration standard was fortified with 5.00 μL of this aqueous internal standard by addition from a 5-μL syringe directly into the 5-μL syringe containing the sample or standard. Samples and calibration standards were mixed before injection into the purge vessel using a 0.2 to 0.3 mL air bubble which was also injected into the purge vessel. Prior to each use of the internal standard spiking solution, about 100 μL was expelled from the 5-mL syringe containing it to assure that the IS spiking solution remained headspace-free.

Analysis of Samples

Calibration standards, unspiked samples, and spiked samples were analyzed using the Method 8030 protocol for purge-and-trap and the GC conditions given above. Three to six replicates of unspiked groundwater were analyzed with each spiked set of samples to define the background levels. In each case, the low spike level and high spike level data sets were acquired in a single day. At the completion of each set of analyses, the pH of an unused sample was measured using a calibrated pH meter equipped with a glass electrode. The following purge-and-trap operating conditions were employed:

Purge Vessel Temperature:	85 ± 2°C; water bath
Purge Conditions:	20 mL/min helium; 15 min; trap temperature less than 30°C
Trap Desorption Conditions:	Flow controlled helium GC carrier (30 mL/min); 180°C for 1.5 min
Trap Bake Conditions:	20 mL/min helium; 210°C for 10 min
Six-Port Value and Transfer Lines:	130°C

During the 1.5 min trap desorption, the spent groundwater samples were used to rinse the condensate from the upper section of the purge vessel and were then removed by suction using a separate 5-mL gas tight syringe reserved for that purpose. The purge vessel received no other rinse between samples. The 5-mL sample transfer syringe was rinsed after each use with reagent water. When not in use for transferring a sample, the all-glass syringe barrel was kept in an oven at 110°C and the syringe plunger and valve and Luer assembly was kept under running carbon-filtered tap water. At the end of each day, the purge vessel was replaced with a clean one from the 110°C oven, and the Tekmar purge-and-trap apparatus was left in "trap bake" mode overnight with a trap temperature of 150°C.

VALIDATION OF THE PEG EXTRACTION/PURGE-AND-TRAP METHOD

Sample Acquisition and Storage

Sediment from a waste stream settling basin at a chemical plant producing two of the three method parameters was provided to Battelle by the chemical plant personnel. The sample, as provided, was contained in a one gallon metal paint can lined with a plastic bag. The sample was transported on ice to Battelle and stored at 4°C until use.

MDL Sample Preparation

Specially prepared PEG (described above) was spiked with acetonitrile at the 150 µg/L level and with acrolein and acrylonitrile each at the 50 µg/L level by addition of an aqueous stock solution freshly prepared from neat reagent (the final spiked PEG sample was 0.1 percent water). The spiked PEG was immediately bottled headspace-free in ten 1.8-mL vials and stored on ice until analysis on the same day. An aliquot of the PEG used to prepare the spiked sample was reserved as the unspiked sample for the determination of background levels.

Preparation of Spiked Sediment Samples

The 1-gallon sediment sample was homogenized by stirring, and approximately 2-kg were transferred to a clean, wide-mouth 1/2-gallon glass jar with a Teflon-lined screw cap. This 2-kg sample which contained about 30 percent headspace was shaken thoroughly to further homogenize the subsample.

High Spike Level--

A glass tube fixed to a 1-mL gas-tight syringe was used to transfer 2.01 ± 0.03 g of sediment into the bottom of ten 50-mL centrifuge tubes with Teflon-lined screw caps. Two of the samples were reserved as unspiked samples. The remaining eight were spiked at the 50 µg/g level with acrolein and at the 100 µg/g level with acetonitrile and acrylonitrile. The spiked analytes were added to each 2-g sample in a 100-µL aliquot of an aqueous spiking mixture freshly prepared from neat reagents (1.00 mg/mL in acrolein and 2.00 mg/mL in both acetonitrile and acrylonitrile). The unspiked samples received 100 µL of the reagent water used to prepare the spiking stock. The spiking aliquot was evenly layered onto the 2-g sample and allowed to stand at 4°C overnight prior to extraction with PEG. On the following day, 40 mL of vacuum cleaned and helium purged PEG was added to each spiked and unspiked sample. The sample was then extracted by shaking vigorously for one min followed by 30 min of sonication. The samples were then centrifuged at approximately 1500 x g for 40 min. The supernatant was transferred to an 8-mL Teflon-lined screw cap vial and stored on ice until analysis on the same day.

Low Spike Level--

Sediment samples were prepared for the low spike level as described above for the high spike level except that the samples were mixed with a vortex mixer for 0.5 minute before overnight storage. The spiking level was 15 µg/g for acetonitrile and 5 µg/g for both acrolein and acrylonitrile and was added as a 10.0 µL aliquot of an aqueous stock freshly prepared from neat reagent. The aqueous spiking stock contained acetonitrile at the 3.00 mg/mL level and acrolein and acrylonitrile at the 1.00 mg/mL level.

Purge-and-Trap Analysis of PEG Extracts

PEG extracts of spiked samples and unspiked samples for a given spiking level, PEG reagent blanks, and PEG-containing calibration standards were analyzed on the same day using the procedures and conditions described above for the groundwater purge-and-trap analyses. Relevant experimental details of the PEG extract analysis which are not found in the appendices or prior discussions are given below.

Calibration standards were prepared by adding 200 µL of blank PEG, which was from the same batch as that used for sample extraction, an appropriate amount of calibration standard solution (see chart below), and 5.00 µL of IS solution to 5.0 mL of reagent water in the sampling syringe.

Calibration Standard Level, µg/g(a,b)	Volume of 10/5/5 mg/L(a) Spiking Stock Used, µL	Concentration in the Purged 5.0 mL Sample mg/L(a)
2/1/1	2	4/2/2
6/3/3	6	12/6/6
20/10/10	20	40/20/20
60/30/30	60	120/60/60
200/100/100	200	400/200/200

(a) Analytes are listed in the order: acetonitrile/acrolein/acrylonitrile.

(b) Referenced to a 2-gm sample extracted with 40 mL of PEG and a 200 µL aliquot of the PEG extract analyzed.

After thorough mixing using an air bubble, the sample and air bubble were transferred to the purging vessel and analyzed exactly as described above for groundwater validations. Sample preparation for purging of unspiked and spiked PEG extracts as well as PEG reagent blanks was performed analogously except that addition of calibration standard solution was omitted. The 200-µL PEG aliquot was measured using a 250-µL gas tight syringe. The clean, dry syringe was filled from the plunger end with the plunger removed using a disposable pasteur pipet from which the narrow tip had been removed. This sample measurement system eliminated possible losses of analytes due to the application of significant subambient pressures to the viscous PEG extracts. After the completion of sample purging, a modified procedure from that described for groundwater samples was used to remove the spent sample and prepare the purge vessel for the next sample. This modified procedure was required since accidental movement of PEG into the purge tube outlet caused unpredictable performance: (1) the spent sample was removed by suction as above for groundwater; (2) 5-mL of reagent water was injected into the purge vessel; (3) the purge vessel outlet was disconnected and the vessel was rinsed by shaking while stoppering the outlet with a finger; (4) the outlet tube was reconnected and the spent rinse was removed by suction as above. This rinse procedure was also completed during the 1.5 min trap desorption so that the empty, rinsed purge vessel was further flushed at 85°C by the 20 mL/min purge flow during the 10-min trap bake cycle.

VALIDATION OF THE DIRECT LIQUID INJECTION METHOD

Sample Acquisition and Storage

The nonaqueous liquid organic waste used was one previously supplied to Battelle for another EPA research program. It was a black, ink-like, low-viscosity mixture of chlorinated hydrocarbons with a density of 1.25 gm/mL. The principal constituents previously identified by Method 624 were dichloroethane, trichloroethane, and tetrachloroethane isomers, and numerous other halogenated C_2 and C_3 isomers were also present. The sample had been in storage at 4°C at Battelle since it was received in 1983.

MDL Sample Preparation

The sample used for the MDL determination was toluene spiked at the 3.00 μg/mL level in all three analytes. Three calibration standards in toluene were prepared in which the three analytes were present at the 2.00, 6.00, and 20.0 μg/mL levels. The MDL sample and the three calibration standards were prepared on the same day as analysis by dilution from a toluene stock solution freshly prepared from the neat reagents. The stock solution contained each analyte at the 2.00 mg/mL level.

Preparation of Spiked Liquid Organic Waste Samples

Nonspiked Liquid Waste--

The liquid waste sample was used as received for the unspiked validation.

High Spike Level--

A 100-gm sample of liquid waste was spiked with the neat analytes at the 100 μg/g level by the syringe addition of 10.0 mg of each compound directly into the 100-gm sample. The spiking level, expressed in weight/volume terms, was 125 g/mL. The spiked sample was equilibrated at 4°C overnight before analysis.

Low Spike Level--

A fresh spiking stock solution was prepared by adding the following quantities of neat reagent to the liquid waste in a 10-mL volumetric: acetonitrile, 20.0 mg (25.5 μL); acrolein, 20.0 mg (23.7 μL); and acrylonitrile, 100 mg (124 μL). Liquid waste (100 mL) was then spiked with 100 μL of this 2/2/10 mg/mL (acetonitrile/acrolein/acrylonitrile) stock solution to produce a sample spiked with acrylonitrile and acrolein at the 2 μg/mL level and acrylonitrile at the 10 μg/mL level. The spiked sample was stored overnight at 4°C prior to analysis on the following day.

Analysis of Samples

Seven replicate 5.0 μL injections were made of each of the validation samples (MDL, unspiked, high spike, and low spike samples) using the GC conditions described above. All of the analyses of a given spike level were accomplished on the same day along with at least three replicates of calibration standards. Each calibration standard contained all three analytes at the same level. The calibration standard levels used for each validation experiment were 2, 6, and 20 µg/mL for the MDL sample, unspiked and low spike levels, and 20, 60, and 200 µg/mL for the high spike level. In all cases, the calibration standards were prepared on the day of use from a freshly prepared toluene stock solution as described above for the MDL determinations.

VALIDATION OF THE HEATED HEADSPACE METHOD

Sample Acquisition and Storage

One of the matrices used for heated headspace validation was the liquid organic waste described above for the direct liquid injection method validation, and the other waste was the settling pond sediment described above for the PEG extraction/purge-and-trap method validation. Acquisition and storage conditions for these two samples are reported in the respective validation sections above.

MDL Sample Preparation

Buffer (0.5 mM) was prepared by adding 150 mg of disodium citrate dihydrate to 1.0 L of Milli-RO/Milli-Q water followed by pH adjustment to pH 4.5 using 9 M H_2SO_4 and a calibrated pH meter. A spiking stock solution was prepared immediately prior to use by the addition of 20.0 mg of each neat analyte (measured volumetrically, described above) to 10.0 mL of pH 4.5 citrate buffer. This 2.00 mg/mL spiking stock was then used to prepare the MDL sample via dilution of 125 µL of the stock into 250 mL of pH 4.5 buffer for a final concentration of 1.00 µg/mL of each analyte. Twenty individual samples were immediately prepared by pipetting 10.0 mL of the 1.00 mg/L solution into 125-mL serum vials and sealing with crimp caps with Teflon-lined septa seals. Bottles and seals were washed, thoroughly rinsed, and stored at 110°C until just prior to use. The samples, after sealing, were immediately placed on ice for overnight storage before analysis. The 2.00 mg/mL (each analyte) aqueous stock described above was used to prepare the methanol standard addition spiking stock by the addition of 250 µL of the stock to 10.0 mL of methanol giving a final concentration of 50 µg/mL. Thus, the 200 µL standard addition aliquot supplied 10.0 µg of each analyte per 10 mL of sample which doubled the 1.00 µg/mL level already present in the samples. The methanol standard addition stock solution was stored overnight on ice with the samples.

Preparation of Spiked Solid Waste Samples

Nonspiked Solid Waste--

Thoroughly homogenized solid waste was expressed from a 500-mL polyethylene bottle into 125-mL serum vials on a Mettler P-1200 balance to give approximately 10-gm samples (x = 10.24 ± 0.13 gm). The serum vials and septa seals were prepared as described above for the MDL study. The sample was expressed through a 5 cm by 0.5 cm ID Teflon tube inserted through the polyethylene bottle cap in such a fashion that none of the sample coated the sides of the vessel. The samples were immediately capped and stored overnight for analysis as described above for MDL samples. The standard addition methanol spiking stock was prepared on the same day as sample analysis from individual freshly prepared 2.00 mg/mL aqueous stocks (acetonitrile and acrolein) and acrylonitrile neat reagent. The final concentrations in the methanol spiking stock were 50, 250 and 500 µg/mL of acetonitrile, acrolein and acrylonitrile, respectively, so that a 200 µL spiking aliquot provided 1.0, 5.0 and 10.0 µg/gm levels (respectively, as above) in the 10-gm solid waste samples. Thus, as for the MDL samples above, the 200 µL standard addition amount resulted in a doubling of the spiked levels.

High Spike Level, Solid Waste--

Samples were weighed into vials as described above for the unspiked samples to give 18 10-gm samples (x = 10.02 ± 0.07 gm). Before sealing, the 18 samples were spiked with 500 µL of an aqueous spiking solution freshly made from neat reagents. The aqueous spiking solution contained acetonitrile and acrolein at the 2.00 mg/mL level and acrylonitile at the 10.0 mg/mL level so that the spiking level produced was 1.00 mg/10 gm for acetonitrile and acrolein and 5.00 mg/10 gm for acrylonitrile or, 100, 100, and 500 µg/gm, respectively. The samples were sealed and mixed vigorously for about 30 sec in a vortexing motion which prevented spreading the sample over more than about 15 percent of the inside surface area of the vial. Overnight storage prior to analysis was at ice temperature. A methanol standard addition spiking solution was prepared from the neat analytes on the day of sample analysis. This spiking solution contained acetonitrile, acrolein, and acrylonitrile at the 5.0, 5.0 and 25.0 mg/mL level, respectively, so that a 200 µL spiking aliquot into the 10-gm sample added 100, 100, and 500 mg/gm, respectively, thereby doubling the levels in the samples used for the standard addition analysis.

Low Spike Level, Solid Waste--

Twenty 10-gm solid waste samples were aliquoted as described above (x = 10.07 ± 0.22 gm). Each sample was spiked with 100 µL of an aqueous stock solution freshly prepared from neat reagents containing 0.50, 1.00, and 5.00 mg/mL of acetonitrile, acrolein, and acrylonitrile, respectively. Thus, the solid waste spiking levels were 5.0, 10.0, and 50.0 µg/gm, respectively, as above. The 20 sample vials were immediately sealed and stored on ice prior to analysis on the following day. The methanol standard addition solution was prepared on the day of sample analysis from neat reagents to give 0.50, 1.00, and 5.00 mg/mL of acetonitrile, acrolein, and acrylonitrile, respectively. Thus, the 200-µL standard addition amount added 10.0, 20.0, and 100 µg/mL, respectively, of acetonitrile, acrolein, and acrylonitrile, thereby tripling the levels in the samples used for standard addition samples.

Preparation of Spiked Liquid Organic Waste Samples

Nonspike, Liquid Organic Waste--

Twenty 8.9-gm samples for unspiked liquid waste analysis were prepared by pipetting 7.2 mL of liquid waste directly into the 125-mL serum vials. The samples were immediately sealed and stored on ice until analysis on the following day. The methanol standard addition stock solution was prepared from neat reagents on the day of unspiked liquid waste sample analysis and contained acetonitrile, acrolein, and acrylonitrile at the 0.50, 0.50, and 5.00 mg/mL levels, respectively. Thus, the 200-μL standard addition spiking aliquot provided 11.2, 11.2, and 112 μg/gm levels respectively, as above.

High Spike Level, Liquid Organic Waste--

To 250 gm of liquid waste was added 25 mg acetonitrile, 25 mg acrolein, and 125 mg acrylonitrile (each as neat reagent) to provide concentrations of 100, 100, and 500 μg/gm, respectively. After mixing, 20 samples were prepared by pipetting 7.2 mL (8.9 gm) into the 125-mL vial, sealing, and storing on ice until analysis on the following day. The methanol standard addition spiking stock solution was prepared as above for unspiked solid waste and contained acetonitrile, acrolein, and acrylonitrile at the 5.00, 5.00, and 25.0 mg/mL levels, respectively. Thus, the 200-μL standard addition aliquot increased the levels in the 8.9-gm samples by 112, 112, and 560 μg/gm, respectively, of acetonitrile, acrolein, and acrylonitrile.

Low Spike Level, Liquid Organic Waste--

Twenty samples were prepared as described above for the high spike level except that the 250 gm of liquid waste was spiked using a stock solution prepared in the waste from neat reagents. The stock solution contained acetonitrile, acrolein, and acrylonitrile at the 2.50, 2.50, and 12.5 mg/mL levels, respectively, so that 1.00 mL in the 250-gm sample resulted in spiked levels of 10.0, 10.0, and 50.0 μg/gm, respectively, as before. The methanol standard addition spiking solution was prepared by a 10-fold dilution of the methanol standard addition spiking stock used for the high spike level liquid waste above. Thus, this spiking stock contained the three analytes at 0.50, 0.50, and 2.50 mg/mL acetonitrile, acrolein, and acrylonitrile, respectively and the 200-μL standard addition aliquot increased the levels in the 8.9-gm low spike samples by 11.2, 11.2, and 56 μg/gm, respectively.

Analysis of Samples

For all cases, samples of a given spiked set were analyzed on the same day by the same analyst. Samples were totally immersed in a 90 ± 1°C water bath for one hour before sampling. The 200-μL standard addition spike was added to alternate samples immediately prior to immersion in the water bath.

Occasional loss of an analysis replicate required some instances of sequential rather than alternate analysis of a given sample type (i.e., a sample which did or did not receive the 200-µL methanol standard addition spike). However, in all cases, data from a given sample was paired with that from a standard addition counterpart using the chronological order (i.e., the nth standard addition data set was used to calculate the levels found in the nth sample analysis). The GC analysis conditions employed are described above under "Method Modifications." The syringe sampling procedure used was the following:

(1) Position the sample vial with the cap only above the surface of the water bath

(2) Pierce the septum with the clean, dry, room temperature sampling syringe (see "Apparatus" for syringe specification)

(3) Rinse the syringe in the sample once by indexing to 2.0 mL and expelling back into the sample

(4) Index the syringe again to 2.0 mL, withdraw it from the vial, and immediately inject (within 1 to 2 sec) onto the GC column.

Calculation of analyte levels found was according to the usual standard addition procedure:

$$\text{Analyte Level} = \frac{\text{Area (sample)}}{\text{Area(std. addn.)} - \text{Area(sample)}} \times \text{Std. addn. level}$$

where Area(sample) = GC peak area for the analyte in the "sample" chromatogram.

Area(std. addn.) = GC peak area for the analyte in the chromatogram for the sample to which the 200-µL standard addition spike was added.

Std. addn. level = The amount the level of the analyte was increased after fortification with the 200-µL standard addition spike (disregarding the added methanol as a sample constituent).

SECTION 5

RESULTS AND DISCUSSION

METHOD MODIFICATIONS

Gas Chromatographic Conditions

Investigations were conducted to identify a GC column which would effectively provide analysis capability for the three method parameters. Both of the columns specified in the 1982 revision of EPA Method 603, on which EPA Method 8030 is based, were found to be unacceptable. Durapak CW400/Porasil C resulted in coelution of acetone and acrolein and such severe peak tailing that low level injections (∿100 ng) did not provide usable data. Chromosorb 101 resulted in exact coelution of acrolein and acetonitrile and partial resolution of acetone from acrylonitrile but otherwise, it performs adequately for acrolein and acrylonitrile in the absence of acetonitrile. Examples of the unacceptable performance of these two GC packings are shown in Figure 1 (Durapak/CW400) and Figure 2 (Chromosorb 101). Other column packings were tried and the following results obtained were: 1 percent SP-1000/Carbopack B (moderate tailing and acrolein-acetone coelution); 0.2 percent CW 1500/Carbopack C (inadequate retention and severe peak tailing); and Chromosorb 104 (high temperature of elution, unacceptable isothermal elution time for acetonitrile and moderate tailing). A brief examination of recent chemical literature revealed a published application for the target analytes using Porapak QS GC packing (1). Testing this packing suggested that a 10-ft column would be required to maintain a comfortable margin of chromatographic resolution between acetonitrile and acrolein and selected potential interferences. No experiments were performed to examine GC performance as a function of carrier flow rate since the 80-100 mesh 10-ft column already generated 36 to 42 psi at room temperature and 30 mL/min. The Porapak QS column packing used in this work was the only one tested which provided baseline separation between the method analytes as well as two potential interferences of interest to EPA (acetone, which elutes between acrolein and acrylonitrile, and methylene chloride, which elutes between methanol and acetonitrile) and also provided good GC peak shape at low levels. Numerous example chromatograms illustrating the performance of Porapak QS in this study are included in the discussion of the method validation results which follow.

Purge-and-Trap Conditions

In the initial work on this program, some experiments were performed to compare method performance using the trap desorption conditions recommended by EPA Method 5030 and those used for this work which were recommended by EMSL-CI (2). Standards containing 30 µg/L of each analyte were analyzed in triplicate using the desorption conditions specified by EPA Method 5030 and those recommended by EMSL-CI. The desorption conditions used in the validation analyses (180°C/1.5 min) resulted in slightly reduced recoveries (4 to 8 percent) compared to the EPA Method 5030 conditions (100°C/2.0 min) but significantly better relative standard deviations (RSDs): 1.1, 1.2, and 1.2 percent for the 180°C/1.5 min conditions compared to 9.3, 8.0, and 1.8 percent for the 100°C/2.0 min conditions for acetonitrile, acrolein, acrylonitrile, respectively. In summary, the 180°C/1.5 min desorption conditions gave improved peak heights for acetonitrile and acrolein which resulted in better reproducibility due, apparently, to the more rapid delivery of trapped analytes to the GC column. The small difference in recoveries probably is not significant since they are less than the observed standard deviations for the 100°C/2.0 min conditions. The trap bake temperature of 210°C was employed since it is generally desirable that the trap bake temperature be higher than the desorption temperature. The low (100°C) desorption temperature specified in EPA Method 5030 was required by the initial GC column temperature of 45°C and the sensitivity of the primary column (Durapak CW400/Porasil C) to the presence of liquid water on the column, which would be introduced by rapid trap heating to 180°C. The Porapak QS column packing is not susceptible to problems caused by liquid water since the initial column temperature (110°C) prevents condensation of water vapor and since macroreticular phases are generally not susceptible to damage caused by liquid water.

LINEAR DYNAMIC RANGE OF THE DETECTOR

The statistical results for the linear dynamic range study using the external standard approach (raw peak areas) are presented in Table 2 for the range tested (0.5 to 500 µg/mL). The external standard linear regression results for each of the three method parameters over the full range and the low range are presented in Table 3. Similarly, statistical and linear regression values resulting from the internal standard calibration approach are shown in Tables 4 and 5, respectively. Linear regression plots for all three analytes at both the full (0.5 to 500 µg/mL) and low (0.5 to 50.0 µg/mL) concentration ranges are shown in Figures 3 through 8. The data set represented by Tables 2 and 3 represents 42 injections of standards and six injections of blanks which were performed on two different days. Thus, the precision values shown in these tables for the 4.0, 15.0, and 50 µg/mL standards (which were repeated on each day and provided overlap for the two ranges) combined data obtained from different calibration standards on separate days and the higher RSD values for those mixed data sets is, therefore, not surprising. Comparing Tables 2 and 4, it is apparent that data processing by the internal standard method results in percent RSD values that are lower by about a factor of 2 for samples analyzed on more than one day compared to the external standard method. In general, the regression line analysis results shown in Tables 3 and 5 and Figures 3 through 5 show excellent linearity of the GC system and FID detector over three orders of magnitude.

VALIDATION OF THE AQUEOUS PURGE-AND-TRAP METHOD

MDL Determination

In a related program for validation of EPA Method 603 (3), the data from the seven replicate analyses of the low spike level in reagent water was used to compute MDL values for acetonitrile, acrolein, and acrylonitrile. The MDL values found were 2.7, 0.7, and 0.5 µg/L using external standard quantification (Table 6) and 2.8, 0.7, and 0.5 µg/L using internal standard quantification (Table 7) for acetonitrile, acrolein, and acrylonitrile, respectively. In similar fashion, when the standard deviations for the low spike level groundwater method validation data (Tables 8 and 9) are used to compute MDL values in that matrix, one obtains 1.7, 0.3, and 0.6 µg/L (external standard method) and 1.8, 0.3, and 0.6 µg/L (internal standard method), respectively, as before. These MDL values for acrolein and acrylonitrile are in good agreement with those presented in EPA Method 8030 (Appendix A), 0.6 and 0.5 µg/L, respectively. Representative chromatograms for a 10 µg/L calibration standard, a reagent water blank, and a low spike level reagent water replicate are presented in Figures 9, 10 and 11, respectively.

Groundwater Analysis Results

The results of replicate analyses of the low spike level groundwater samples are presented in Table 8 with external standard quantification and in Table 9 with internal standard quantification based on 1-chloropropane. Agreement between the two calibration methods is very good. The RSD for all compounds were less than six percent. As for nearly all sample sets analyzed, the RSDs for acetonitrile are significantly higher than those for acrolein and acrylonitrile. The reason for the lower precision for acetonitrile in all determinations appears to be due to the relatively low purging efficiency of this compound, estimated to be 40 to 50 percent.

The results of replicate analyses of the high spike level groundwater samples are presented in Table 10 with external standard quantification and in Table 11 with internal standard quantification based on 1-chloropropane. The RSDs for all compounds were less than seven percent for external calibration, with average recoveries ranging from 85 to 91 percent. Similar results were obtained for the internal standard calibration data. Since background levels for this matrix were extremely low, a full seven replicate unspiked data set was not acquired. Instead, three or more unspiked replicates were analyzed for background level assessment along with the spiked sample sets. As indicated in Figure 12, the background material interfering with acrylonitrile (1.0 to 2.0 µg/L, Tables 8 and 10) does not have the correct GC retention for acrylonitrile.

Representative chromatograms for unspiked, low spike level, and high spike level buffered groundwater samples are presented in Figures 12, 13, and 14, respectively. The pH of the groundwater samples was checked at the completion of analyses for each spike level set. It was found that the citrate buffer added contained insufficient capacity to change the pH to the desired 4.0 to 5.0 range, so that the pH remained near its original value of 6.8. Since the acrolein recoveries were excellent (90 and 95 percent, low and high levels, respectively), overnight storage at pH 6.8 for this matrix apparently did not result in any significant acrolein loss due to decomposition.

VALIDATION OF THE PEG EXTRACTION/PURGE-AND-TRAP METHOD

MDL Determination

The results of replicate analyses of a spiked PEG sample for MDL determination are presented in Table 12 with external standard quantification and in Table 13 with internal standard quantification based on 1-chloropropane. The MDLs determined for the two calibration procedures are essentially equivalent at 1.0 and 1.2 mg/kg, respectively, for acetonitrile, 0.7 and 0.6 mg/kg, respectively, for acrolein and 0.2 and 0.3 mg/kg, respectively, for acrylonitrile. These MDL values were calculated based on an assumed sample size of 2.0 g of sample prepared in a total volume of 40 mL of PEG and a 200-µL aliquot of the PEG taken for analysis. The average recoveries were 100 percent for all analytes with both calibration procedures.

Representative chromatograms for a 10 mg/L calibration standard in PEG, and a spiked PEG extract for MDL determination are presented in Figures 15 and 16, respectively.

Solid Waste Analysis Results

The results of replicate analyses for the PEG extracts of the low spike level solid waste samples are presented in Table 14 with external standard calibration and in Table 15 with internal standard calibration based on 1-chloropropane. Acrolein apparently decomposed in the solid waste sample after storage overnight at ice temperature, and its average recovery was only 10 percent. Average recoveries for acetonitrile spiked at 15 mg/kg and acrylonitrile spiked at 5 mg/kg were 97 and 76 percent, respectively, with relative standard deviations of less than 10 percent in both cases.

The results of replicate analyses of the PEG extracts of the high spike level solid waste samples are presented in Table 16 with external standard calibration and in Table 17 with internal standard calibration based on 1-chloropropane. As for the low spike level samples, acrolein was lost due to apparent decomposition in these high spike level samples, while the average recoveries for acetonitrile and acrylonitrile, both spiked at the 100 mg/kg level, were 96 and 84 percent, respectively. Representative chromatograms of unspiked solid waste PEG extract, a low spike level, and a high spike level solid waste PEG extracts are presented in Figures 17, 18, and 19, respectively.

The lower recoveries for acrylonitrile in this matrix (76 and 84 percent for low and high spike levels, respectively) can be attributed to irreversible adsorption or to decomposition since a recovery of 100 percent was observed for the MDL data set. Certainly, this hypothesis is consistent with the essentially quantitative loss of spiked acrolein for this matrix.

Significant difficulties encountered with PEG cleanup were noted above under the discussion of Method Modifications. A chromatogram showing a PEG blank analysis for the most interference-free batch of PEG among the three that were prepared is given in Figure 20. The GC peak eluting just prior to acrylonitrile with a retention time equivalent to acetone was variable from one batch to another, with the worst case resulting in a peak about the same size as the internal standard. Another difficulty encountered with the PEG extract/purge-and-trap method was probably caused by the movement of PEG droplets into the purge-and-trap apparatus. Movement of PEG into the valve, trap, and associated transfer plumbing of the purge-and-trap apparatus might be expected to result in significant memory effects and other artifacts, and the observation of such effects on two occasions required trap replacement and complete flushing with reagent water of transfer lines and the six-port valve. An added precaution against movement of PEG droplets into the system was also adopted for recycling the purge vessel between runs; that precaution was described above in Section 4.

In summary, while good results were indeed achieved with the PEG extract approach, significant difficulties were encountered which make the method somewhat more difficult to use and subject to failure in routine use. The option which EPA Method 5030 allows for the use of high-purity methanol is not useful with Porapak QS and FID detection due to the peak tailing of methanol. Even the use of 2 to 3 µL of spiking standards prepared in methanol produced methanol GC peak tails that added significantly to the difficulty of data treatment and required the use of aqueous calibration standards for all of the purge-and-trap work.

VALIDATION OF THE DIRECT LIQUID INJECTION METHOD

MDL Determination

The results of replicate analyses of spiked toluene for MDL determination are presented in Table 18. The MDL values found were 0.8, 0.6, and 0.5 mg/L for acetonitrile, acrolein, and acrylonitrile, respectively. Average recoveries ranged between 97 percent for acrolein to 107 percent for acetonitrile, with relative standard deviations of less than 8 percent in all cases. Representative chromatograms for a 6.0 mg/L calibration standard in toluene and one of the replicate analyses of the spiked toluene sample for MDL determination are presented in Figures 21 and 22, respectively.

Organic Liquid Waste Analysis Results

The results of replicate background determinations for the organic liquid waste are presented in Table 19. The average values obtained were used in Tables 20 and 21 for correction of the spiked samples for background levels of analyte in order to calculate average percent recoveries.

The results of replicate analyses of low spike level organic liquid waste are presented in Table 20, and the high level spiked organic liquid waste results are presented in Table 21. Recoveries for the low level spiked waste ranged from 86 percent for acetonitrile to 111 percent for acrylonitrile, and all relative standard deviations were less than 4 percent. For the high spike level liquid organic waste samples, recoveries ranged from 98 percent for acrylonitrile to 109 percent for acetonitrile, with relative standard deviations of 11 to 12 percent in all cases.

Representative chromatograms for unspiked, low spike level, and high spike level liquid organic waste are presented in Figures 23, 24, and 25, respectively. As indicated in Figure 23, there are two background species, neither of which are acrylonitrile, but which are always included in spiked sample GC peak integrations for acrylonitrile. The background level given in Table 18 for acrylonitrile is for both of these species.

The only difficulty encountered in the direct liquid injection method validation work was late eluting sample constituents. The 5-µL liquid organic waste injections required a minimum of 40 min at 230°C to achieve a reasonably steady baseline for subsequent sample analysis. When a different liquid organic waste which contained about 10 to 30 percent kerosene was analyzed, the time required to clean the column of late-eluting material was so lengthy that work on that matrix was halted. While the upper temperature limit for Porapak QS is 250°C, lengthy hold times at the temperature limit is not advisable. The presence of water in matrices of this type (liquid organic wastes) is not anticipated to be a problem. Thus, a thick film apolar column packing such as OV-101 or SP-2100 or a similarly coated capillary column would probably be a more effective way to approach the direct liquid injection analysis of an organic waste such as the one used for validation since this type of column could be more easily cleaned of late eluting sample constituents. Of course, Porapak QS would remain the column packing of choice for direct aqueous injection of groundwater samples.

VALIDATION OF THE HEATED HEADSPACE METHOD

MDL Determination

The results of replicate analyses for MDL determinations of spiked reagent water samples are presented in Table 22. The MDL values found were 1, 0.3, and 0.4 mg/L for acetonitrile, acrolein, and acrylonitrile, respectively. The percent recoveries and percent RSDs found were 110 ± 33, 60 ± 16 and 60 ± 20, respectively, for acetonitrile, acrolein, and acrylonitrile. The chromatogram for one of the MDL samples is shown in Figure 26. The chromatogram of the corresponding sample used for quantification of the Figure 26 data (to which the 200-µL methanol standard addition aliquot had been added) is shown in Figure 27.

Solid Waste Analysis Results

The results of replicate background determinations for the unspiked solid waste by the heated headspace method are presented in Table 23. The average values obtained for acetonitrile and acrylonitrile (0.6 and 11 mg/kg, respectively) were used to correct the levels found for the spiked solid waste samples (Tables 24 and 25) in order to calculate average percent recoveries of the spiked analytes. Example chromatograms for the analysis of unspiked solid waste are shown in Figure 28 (sample without the standard addition spike) and Figure 29 (sample with the 200-µL methanol standard addition aliquot). As before for the MDL example, the analysis depicted in Figure 29 was used to quantify that of Figure 28.

Since acrolein apparently decomposed in spiked samples either during the overnight storage at ice temperature or during the 1-h equilibrations at 90°C, the acrolein results are not meaningful, and acrolein values are not shown in Tables 23, 24 and 25. Results for the low spike level samples (Table 24) yield percent recoveries and percent RSDs of 46 ± 48 and 51 ± 32 for acetonitrile and acrylonitrile, respectively. The corresponding values for the high spike level samples (Table 25) were 120 ± 65 and 76 ± 20, respectively, for acetonitrile and acrylonitrile. The high percent RSD values (20 to 80 percent) observed for the MDL and solid waste data sets (Tables 22 through 25) can be attributed to variability in the headspace sampling and injection procedure. When sampling headspace in equilibrium at 90°C with a wet sample, a significant but variable amount of liquid, estimated to be 50 to 200 µL, condenses in the 5-mL sampling syringe which is at room temperature. Upon injection of the sample, a variable amount of this condensate, which is certainly more enriched in the spiked analytes than is the vapor, is delivered to the GC column. When sampling the 125-mL vials to which had been added the 200-µL methanol spiking aliquot is for standard addition quantification, the condensation problem was somewhat more severe. The greater amount of liquid sample injected for these standard addition samples accounts for the generally low recovery values found. Example chromatograms for analysis of the low spike level are shown in Figure 30 (sample without the standard additon spike) and Figure 31 (sample with the 200-µL methanol standard addition aliquot). Corresponding example chromatograms for the high spike level are shown in Figures 32 and 33. The Figure 31 chromatogram is for the standard addition analysis used to quantify the analysis depicted in Figure 30. Figure 32 is similarly related to Figure 31.

Liquid Organic Waste Analysis Results

The results of replicate background determinations for the liquid organic waste by the heated headspace method are presented in Table 26. As described above for the solid waste, acrolein was not stable in this matrix, and, therefore, no analysis results are given for acrolein for the spiked and unspiked samples. The average background levels found for acetonitrile and acrylonitrile (0.4 and 7 mg/kg) were used to correct the levels found for the spiked solid waste samples (Tables 27 and 28) in order to calculate average percent recoveries of the spiked analytes. Example chromatograms for the unspiked liquid waste analyses are shown in Figure 34 (sample without the standard addition spike) and Figure 35 (sample with the 200-µL methanol standard addition aliquot). The data for the analysis depicted in Figure 35 was used to quantify that of Figure 34.

Results for the low spike level liquid organic waste samples (Table 27) yield percent recoveries and percent RSDs of -20 ± 1900 and 40 ± 2100 for acetonitrile and acrylonitrile, respectively. The corresponding values for the high level spike (Table 28) are 700 ± 110 and 250 ± 1300, respectively, as before. The extremely poor accuracy and reproducibility observed for these samples is due to the problem of sample condensation in the 5-mL syringe during headspace sampling which was described above for the solid waste samples. However, in this case, the low boiling point of the sample severely aggravated this problem compared to the solid waste case and thereby resulted in far less reproducible data. In all cases except the unspiked sample set, the two-standard-deviation confidence internal for the average amount found extends to negative values. The large degree of irreproducability encountered for this matrix using the heated headspace approach does not allow even an order-of-magnitude confidence internal in a single replicate analysis protocol. Example chromatograms for the low and high spike levels are shown in Figures 36 through 39. Figure 37 represents the standard addition data which was used to quantify the low spike level replicate of Figure 36, and, analogously, Figure 39 is the standard addition analysis corresponding to the high spike level replicate of Figure 38.

COMPARISON OF VALIDATION RESULTS

The MDL results and percent recovery values for all of the method validation work are collected in Table 29 for the purpose of comparison. The PEG heated purge-and-trap, direct liquid injection and heated headspace sampling all have about the same MDL values for their respective clean matrices (toluene for direct liquid injection and reagent water for the other two). As expected, the MDL values for direct heated purge-and-trap are about 1000-fold lower. Solid waste was analyzed by both PEG/purge-and-trap and heated headspace, and the PEG/purge-and-trap approach is clearly superior in both accuracy and precision for the solid waste used. The liquid organic waste was analyzed by both direct liquid injection and heated headspace, and the former method is clearly the only acceptable one for the matrix used. Poor recovery of acrolein for the solid waste by PEG/purge-and-trap compared with that for groundwater, also, by purge-and-trap suggests that acrolein was either irreversibly adsorbed or decomposed during the 4°C overnight equilibration with the solid waste. In the case of the HHS method, the data clearly indicate that decomposition of acrolein during the 1-hr, 90°C equilibration is a major factor since the standard addition amount of acrolein, added just prior to the 90°C equilibration, is also nearly quantitatively lost.

Conditions

Column: Durapak CW400/Porasil C 100/120 mesh; 6 ft x 2 mm ID
Carrier: Helium at 30 ml/min
Program: 40°C, 2 min; 40°C to 120°C at 8°/min

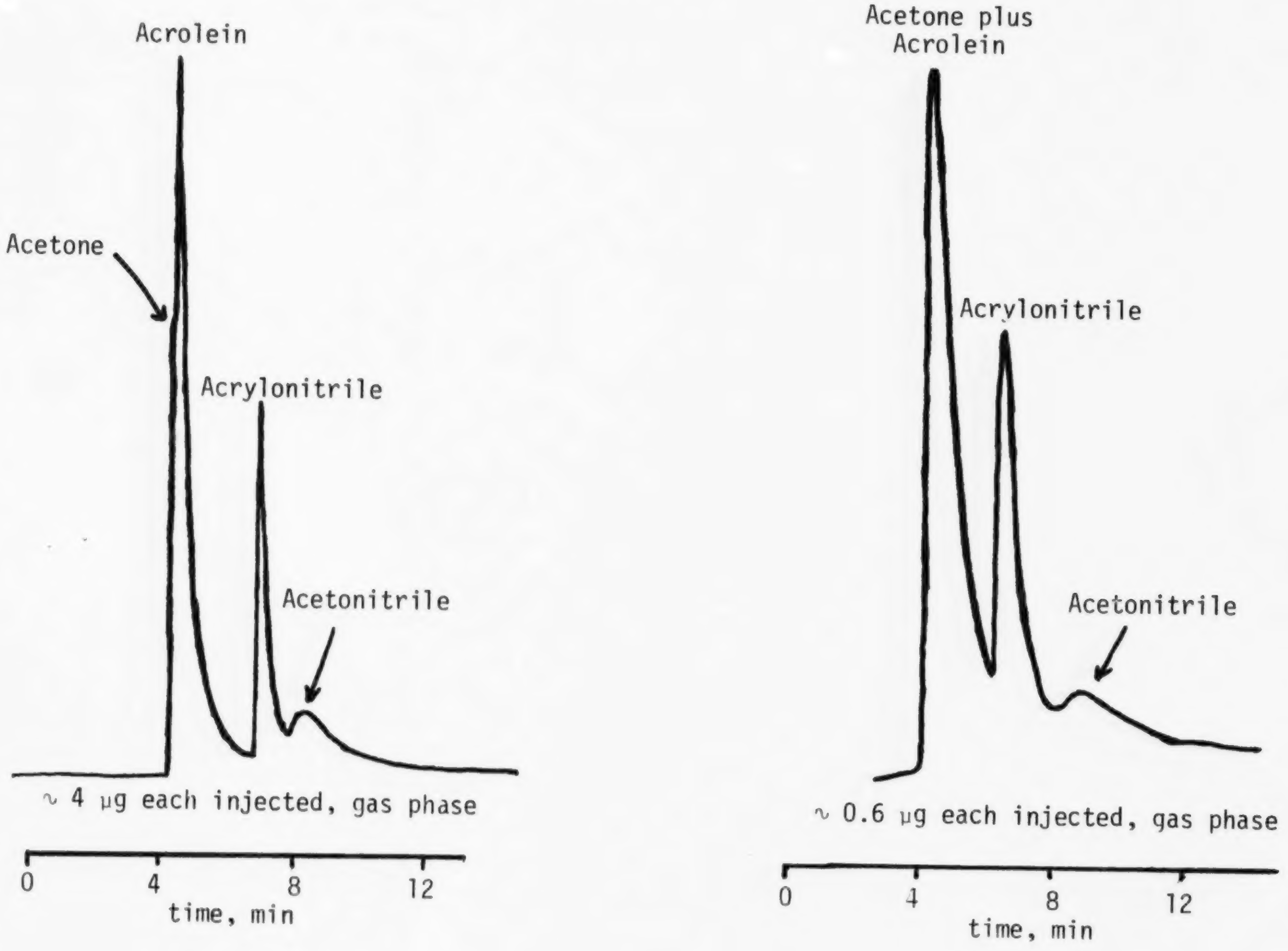
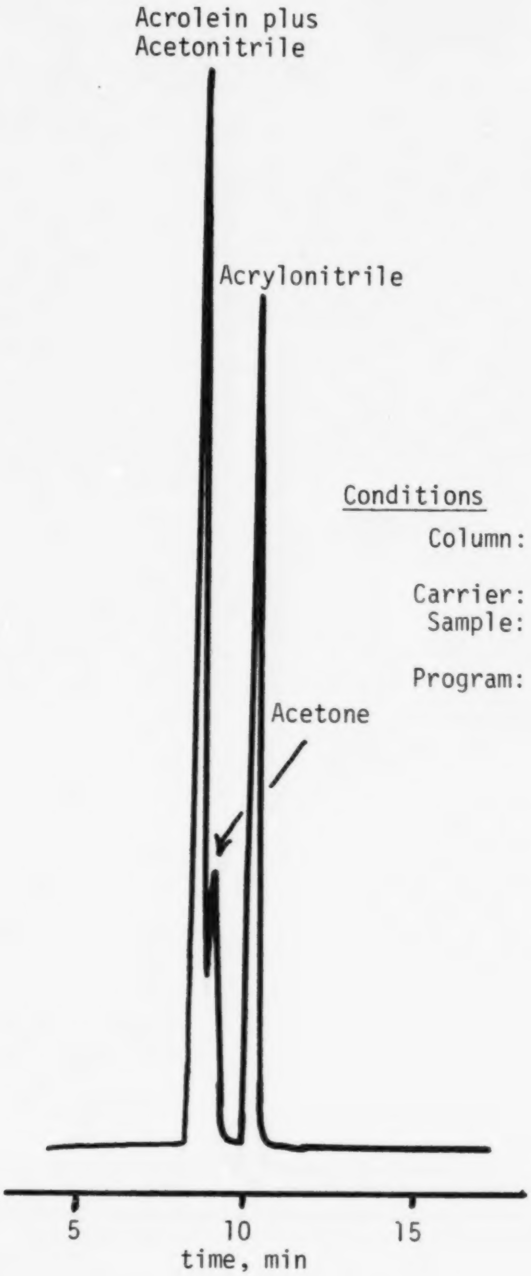


Figure 1. Gas chromatogram of Method 8030 parameters plus acetone on Durapak CW400/Porasil C.



Conditions

Column: Chromosorb 101, 60/80 mesh; 10 ft x 2 mm ID
Carrier: Helium at 30 ml/min
Sample: ∿4 μg each component, gas phase
Program: 80°C, 5 min; 80°C to 150°C at 8°C/min

Figure 2. Gas chromatogram of Method 8030 parameters plus acetone on chromosorb 101.

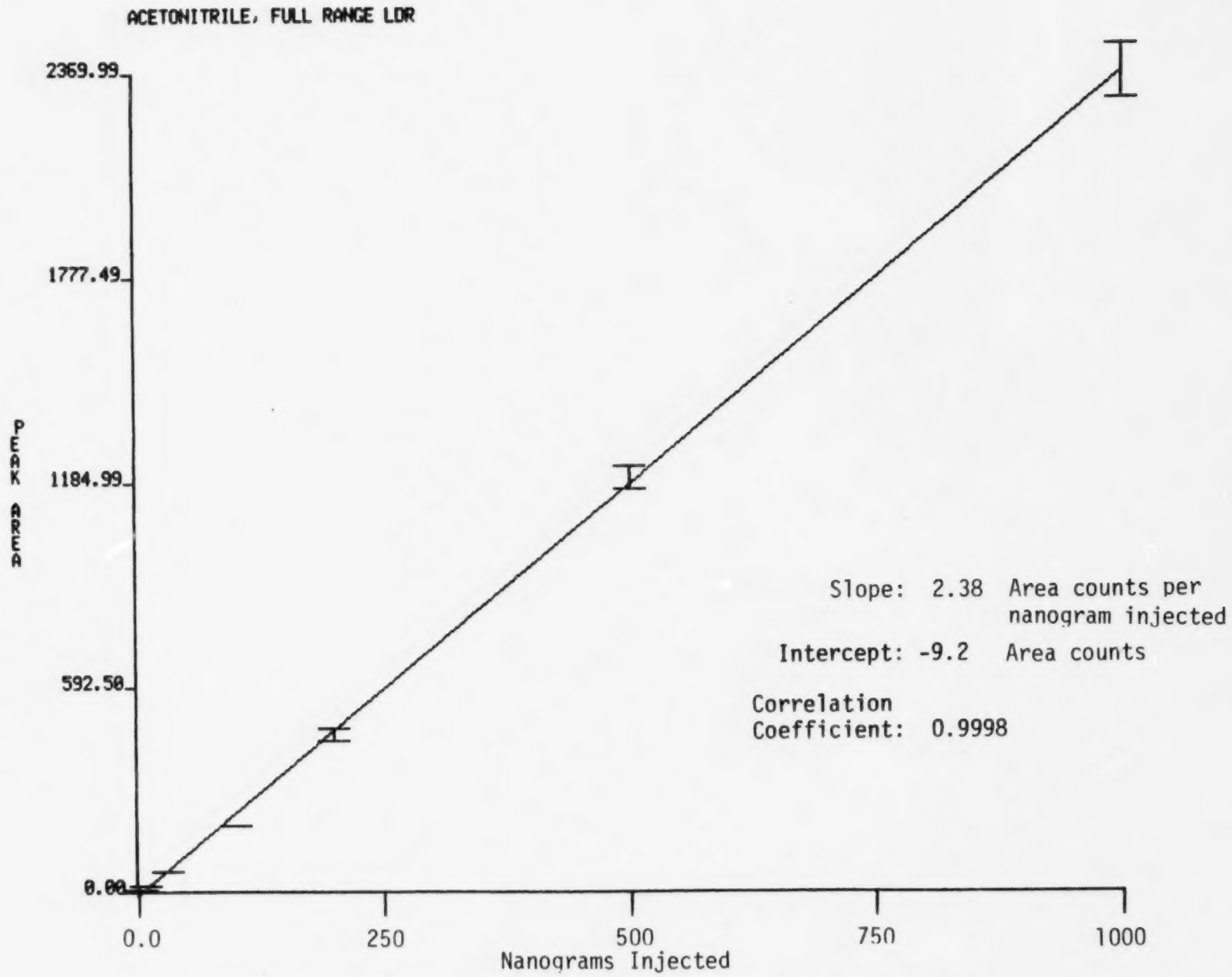
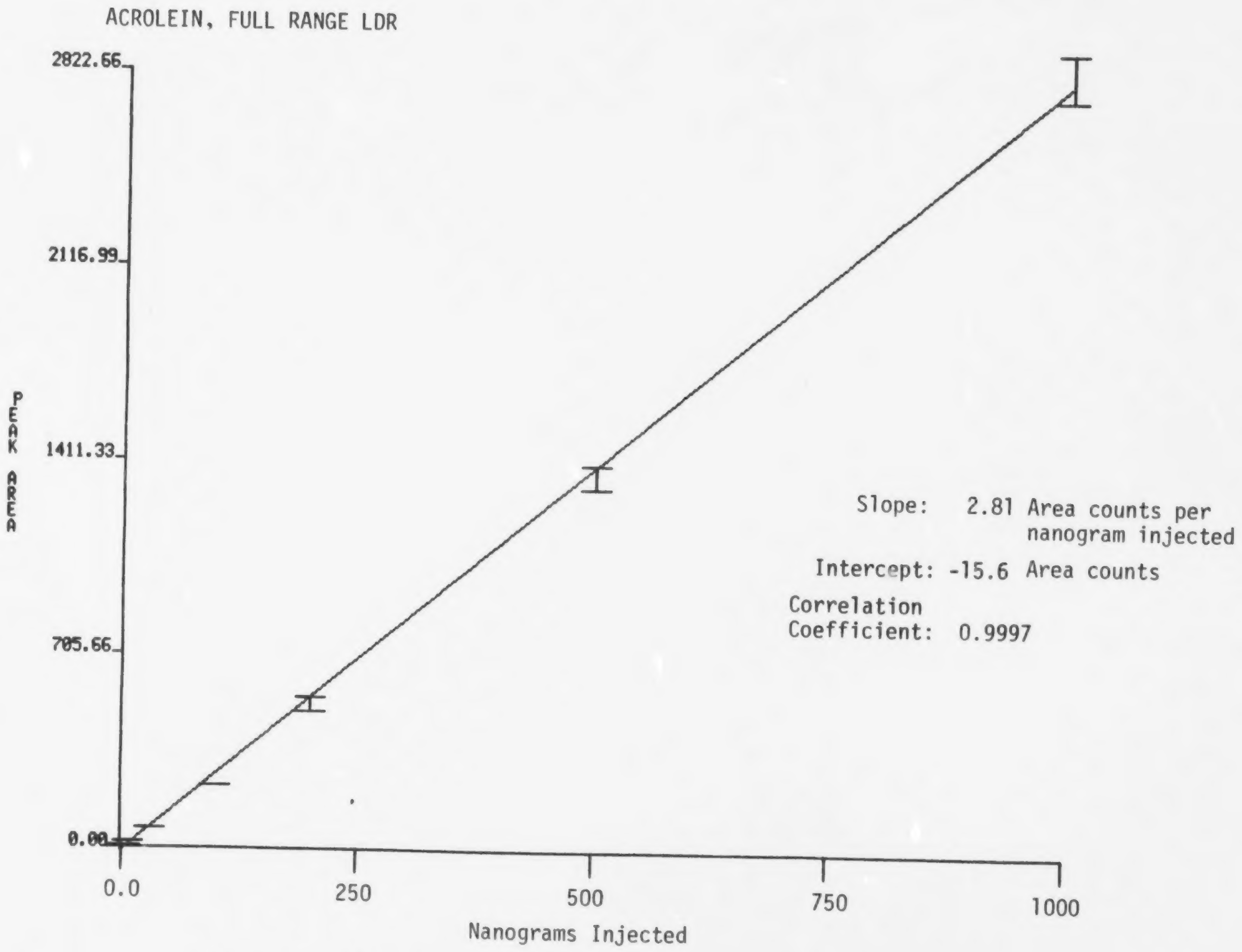


Figure 3. Linear regression analysis plot for linear dynamic range of acetonitrile, 0.5 to 500 mg/L, 2 μL injection.



Slope: 2.81 Area counts per nanogram injected

Intercept: -15.6 Area counts

Correlation Coefficient: 0.9997

Figure 4. Linear regression analysis plot for linear dynamic range of acrolein, 0.5 to 500 mg/L, 2 μL injection.

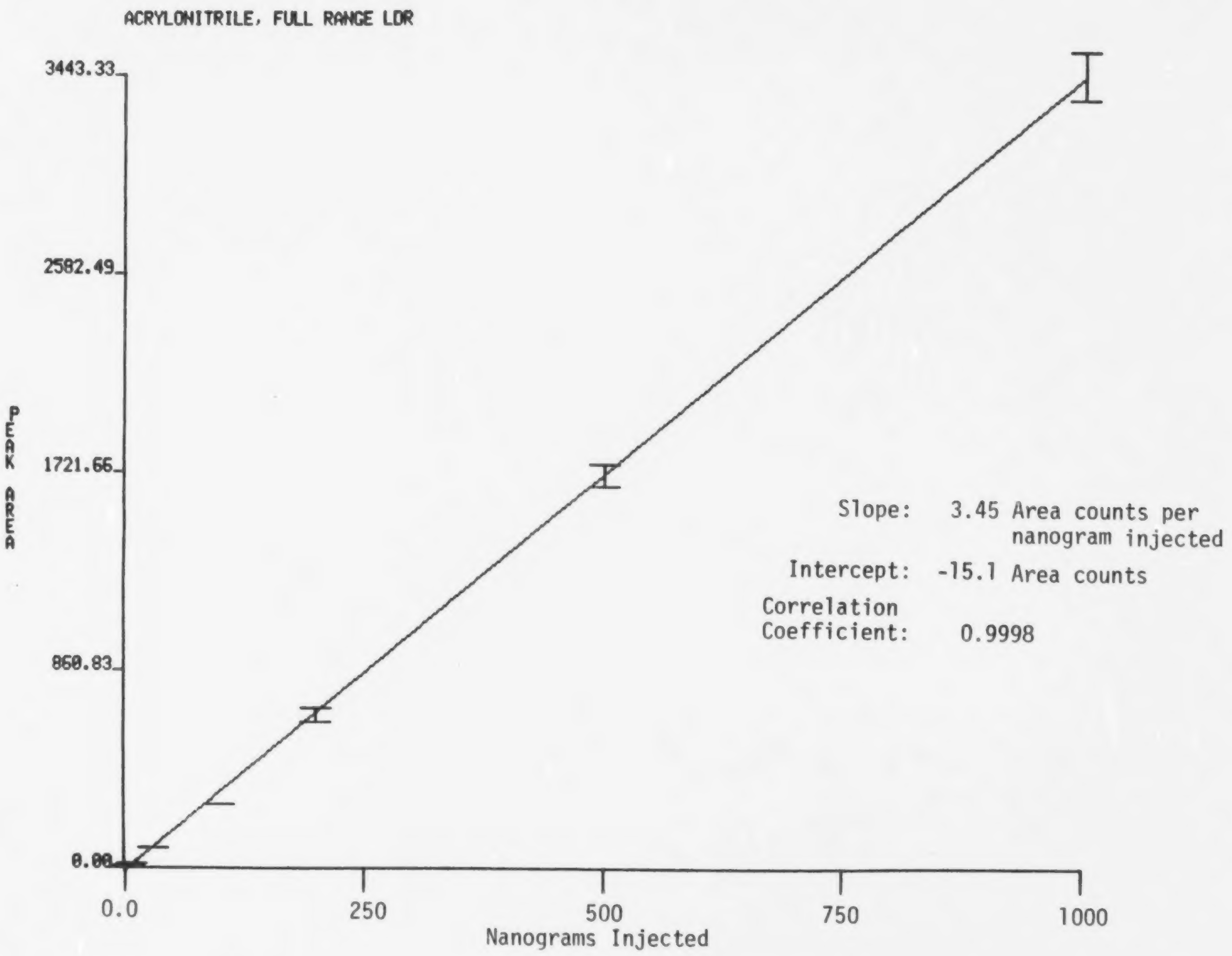
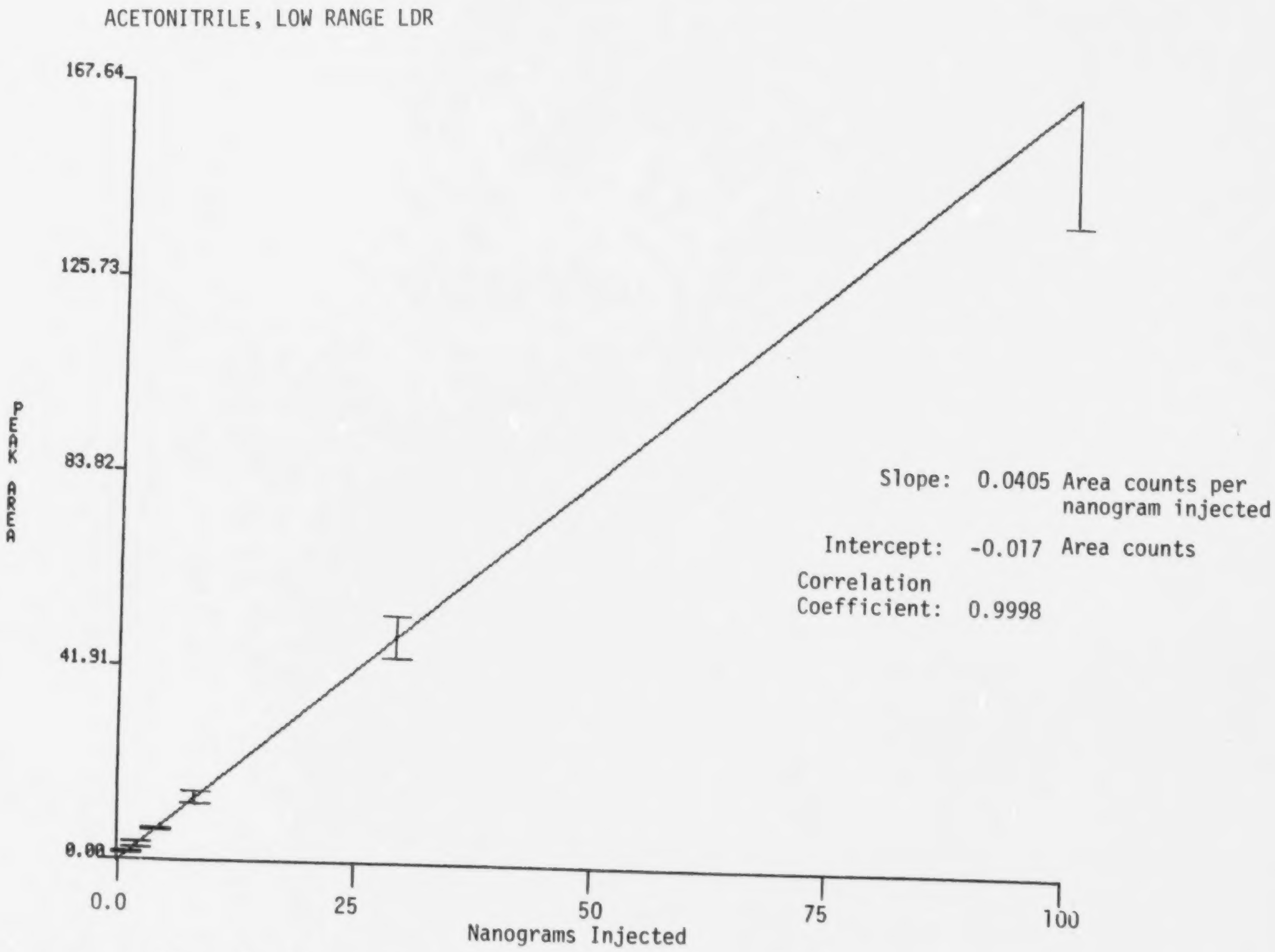


Figure 5. Linear regression analysis plot for linear dynamic range of acrylonitrile, 0.5 to 500 mg/L, 2 μL injection.

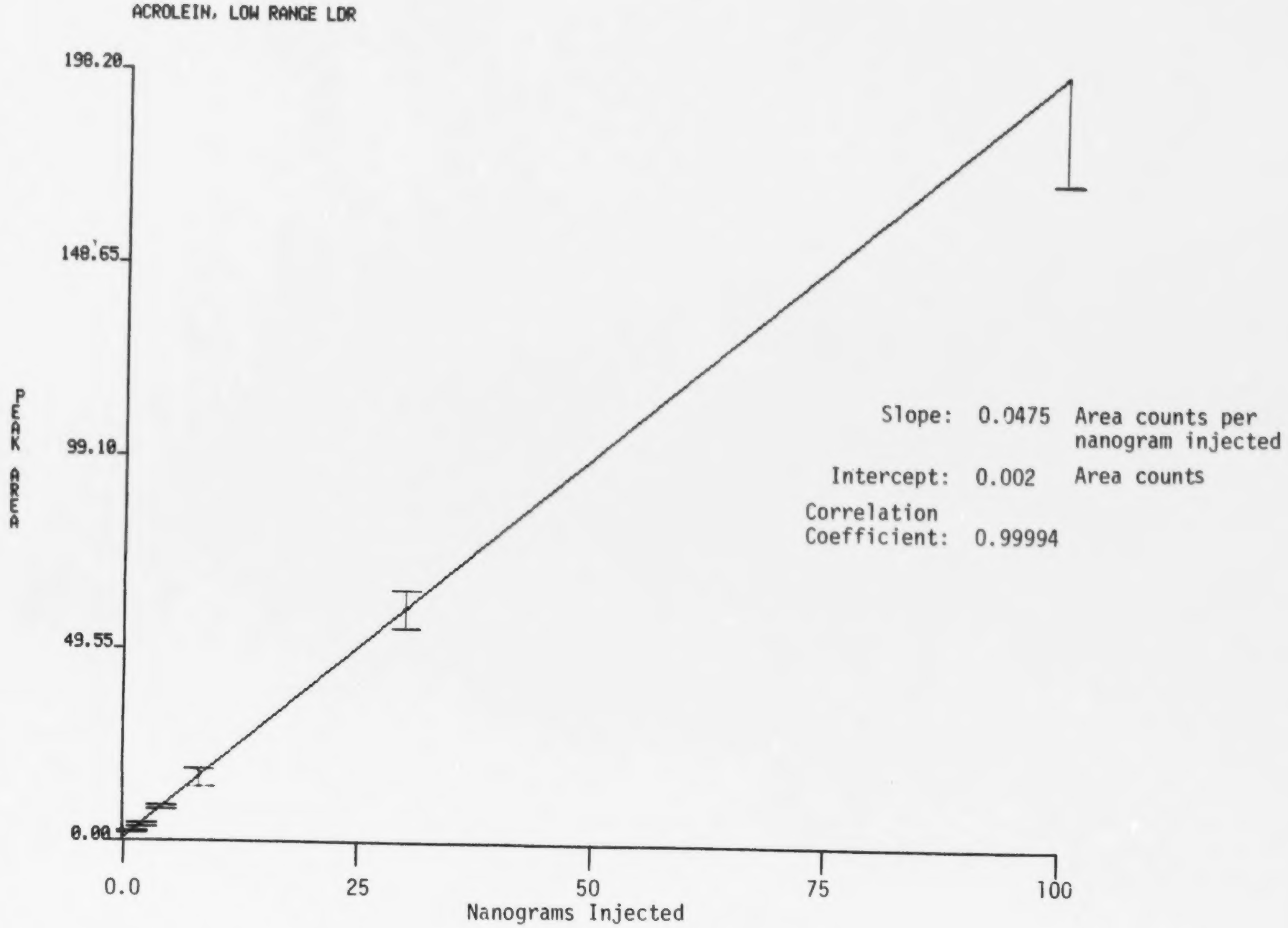


Slope: 0.0405 Area counts per nanogram injected

Intercept: -0.017 Area counts

Correlation Coefficient: 0.9998

Figure 6. Linear regression analysis plot for low range linear dynamic range of acetonitrile, 0.5 to 50 mg/L, 2 μL injection.



Slope: 0.0475 Area counts per nanogram injected

Intercept: 0.002 Area counts

Correlation Coefficient: 0.99994

Figure 7. Linear regression analysis plot for low range linear dynamic range of acrolein, 0.5 to 50 mg/L, 2 μL injection.

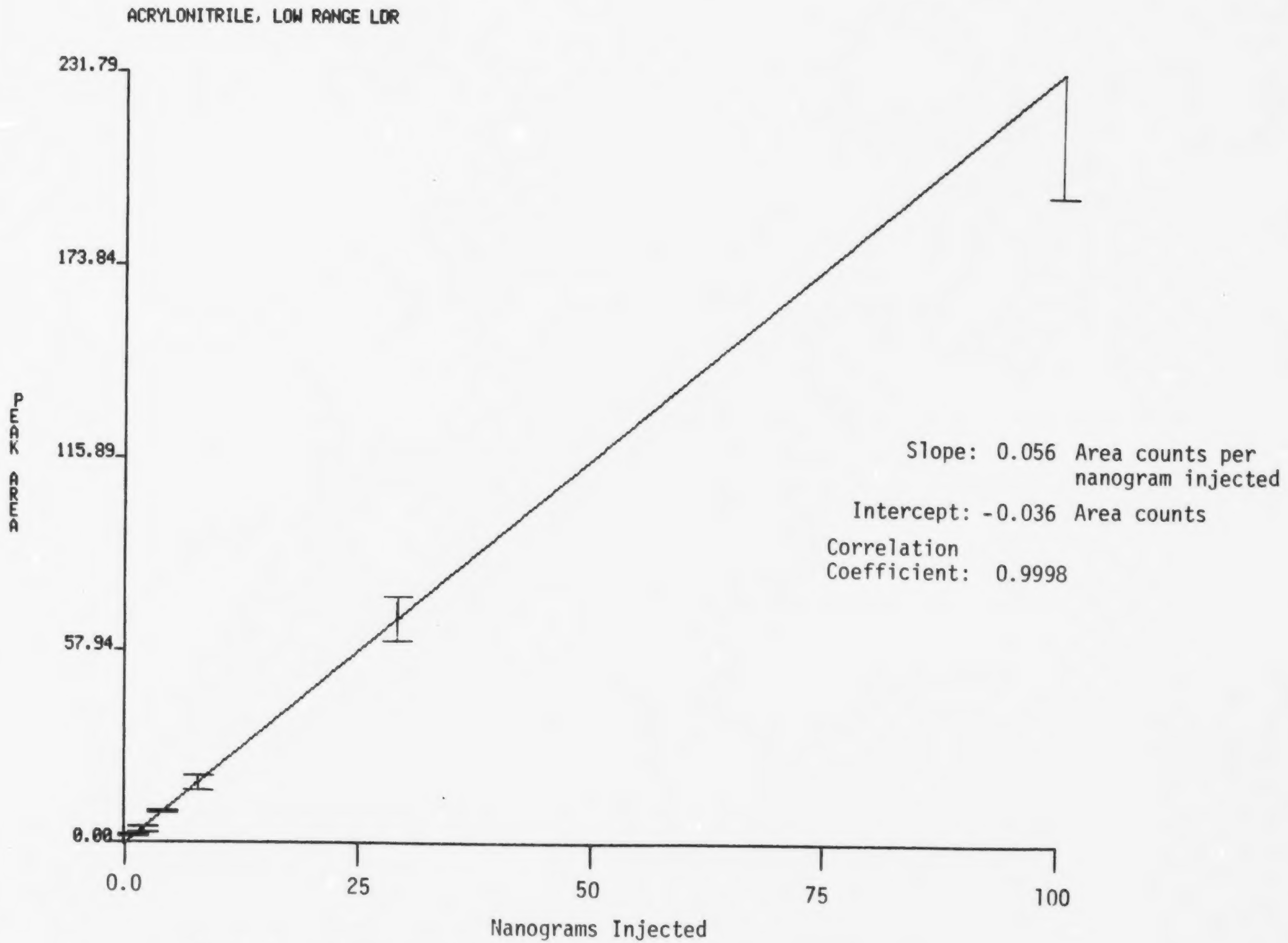


Figure 8. Linear regression analysis plot for low range linear dynamic range of acrylonitrile, 0.5 to 500 mg/L, 2 μL injection.

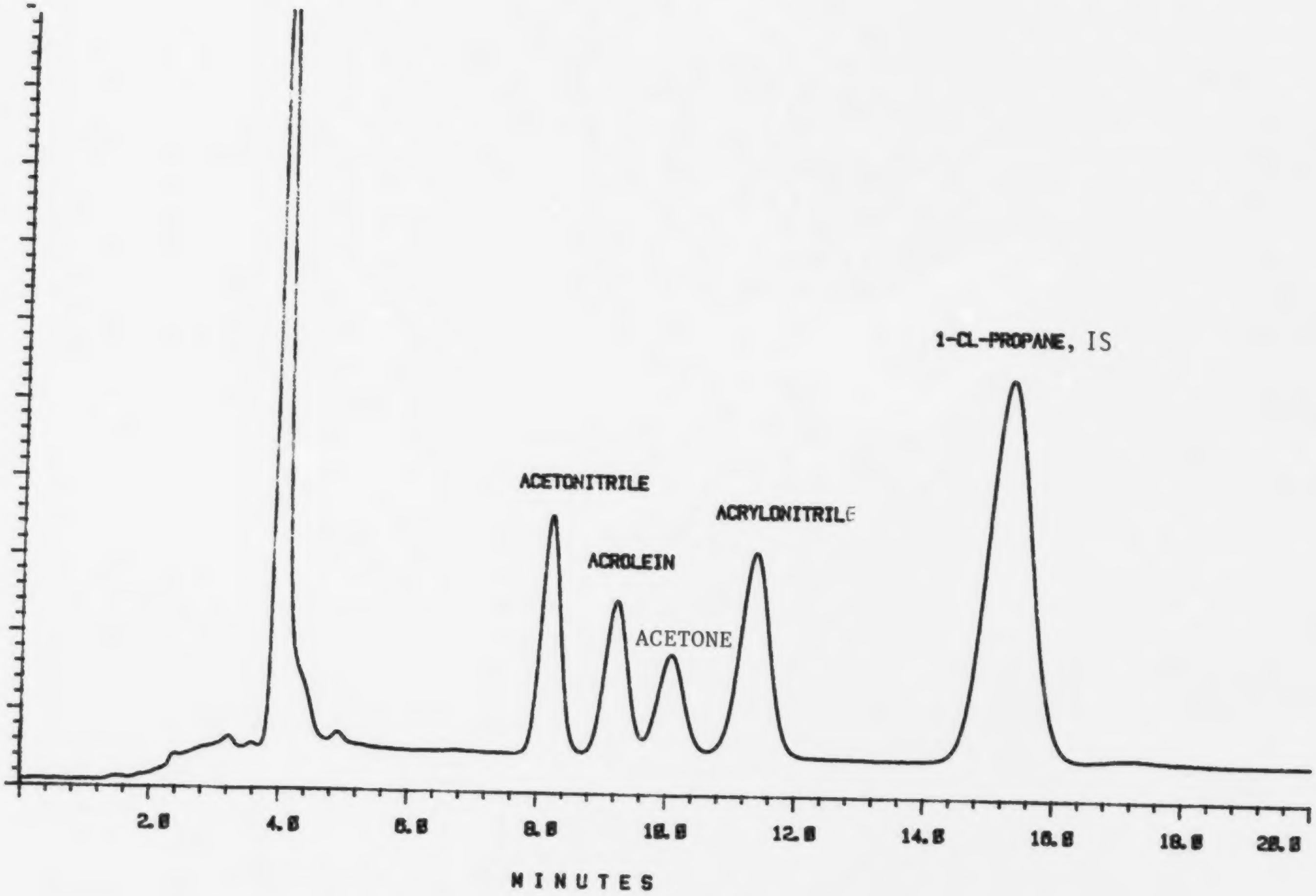


Figure 9. GC-FID chromatogram of a 10 µg/L calibration standard analyzed using modified Method 8030 and Method 5030.

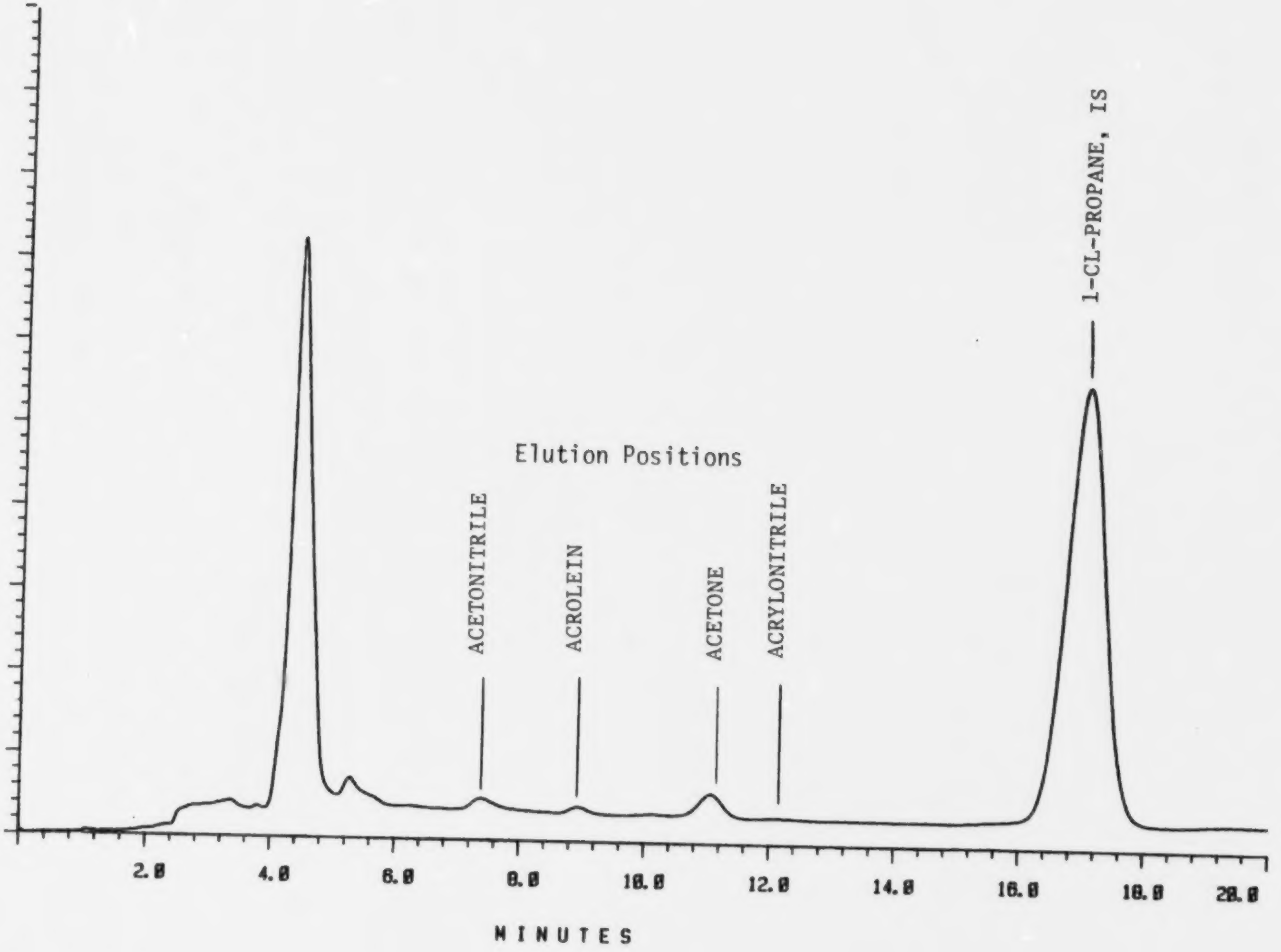


FIGURE 10. GC-FID chromatogram of a reagent water blank analyzed using modified Method 8030 and Method 5030.

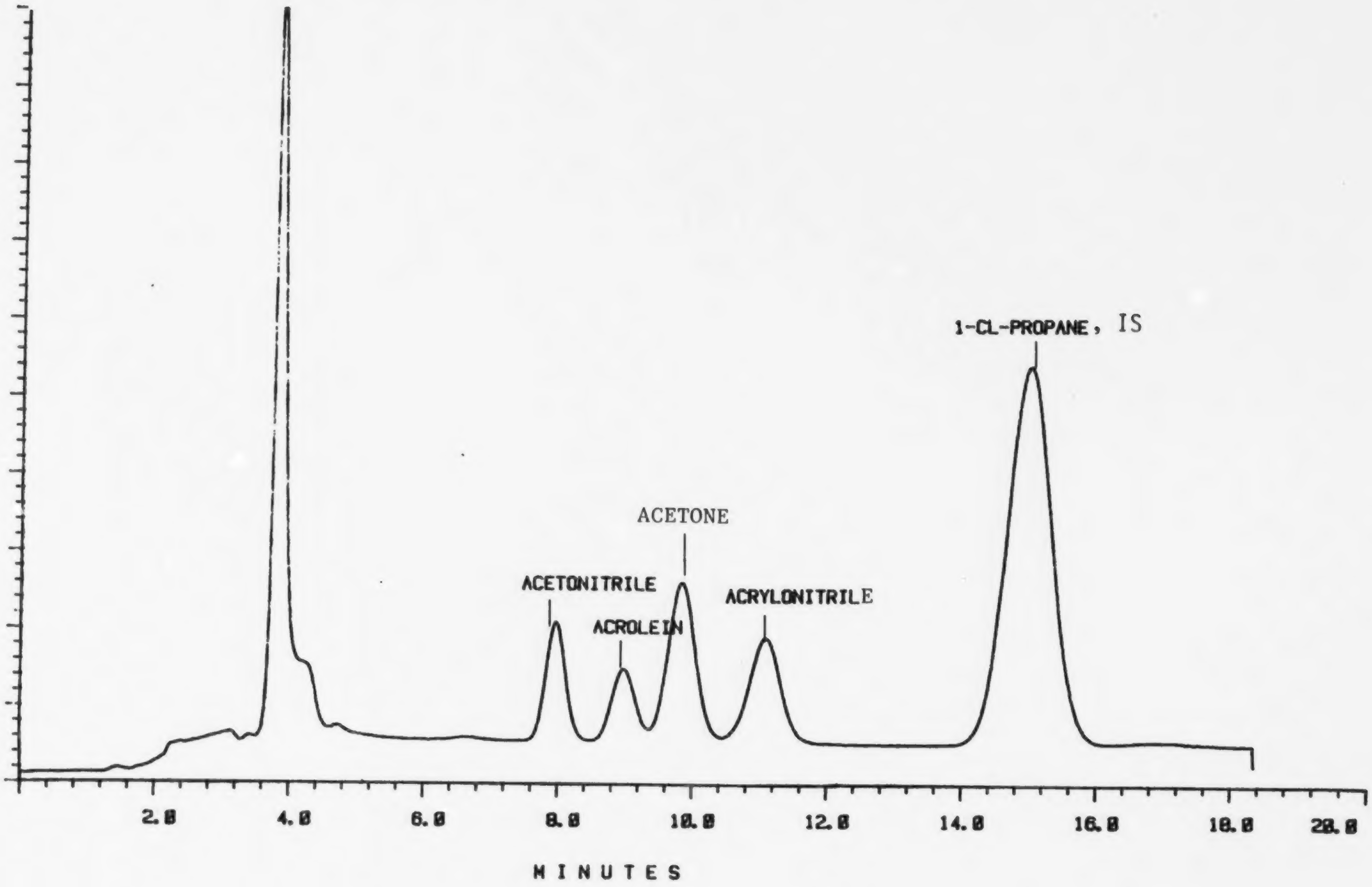


Figure 11. GC-FID chromatogram of low spike level reagent water using modified Method 8030 and Method 5030.

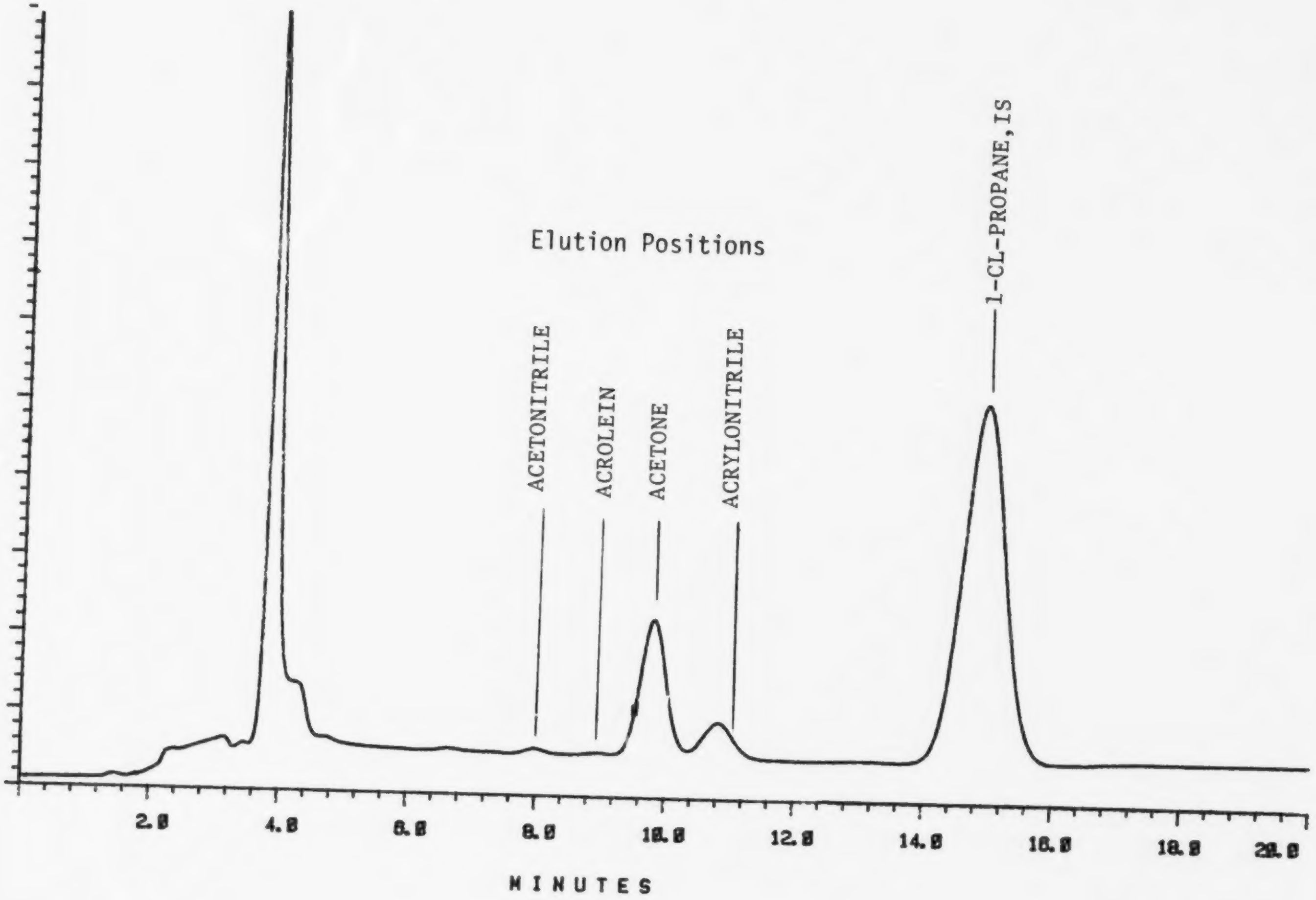


Figure 12. GC-FID chromatogram of unspiked groundwater analyzed using modified Method 8030 and Method 5030.

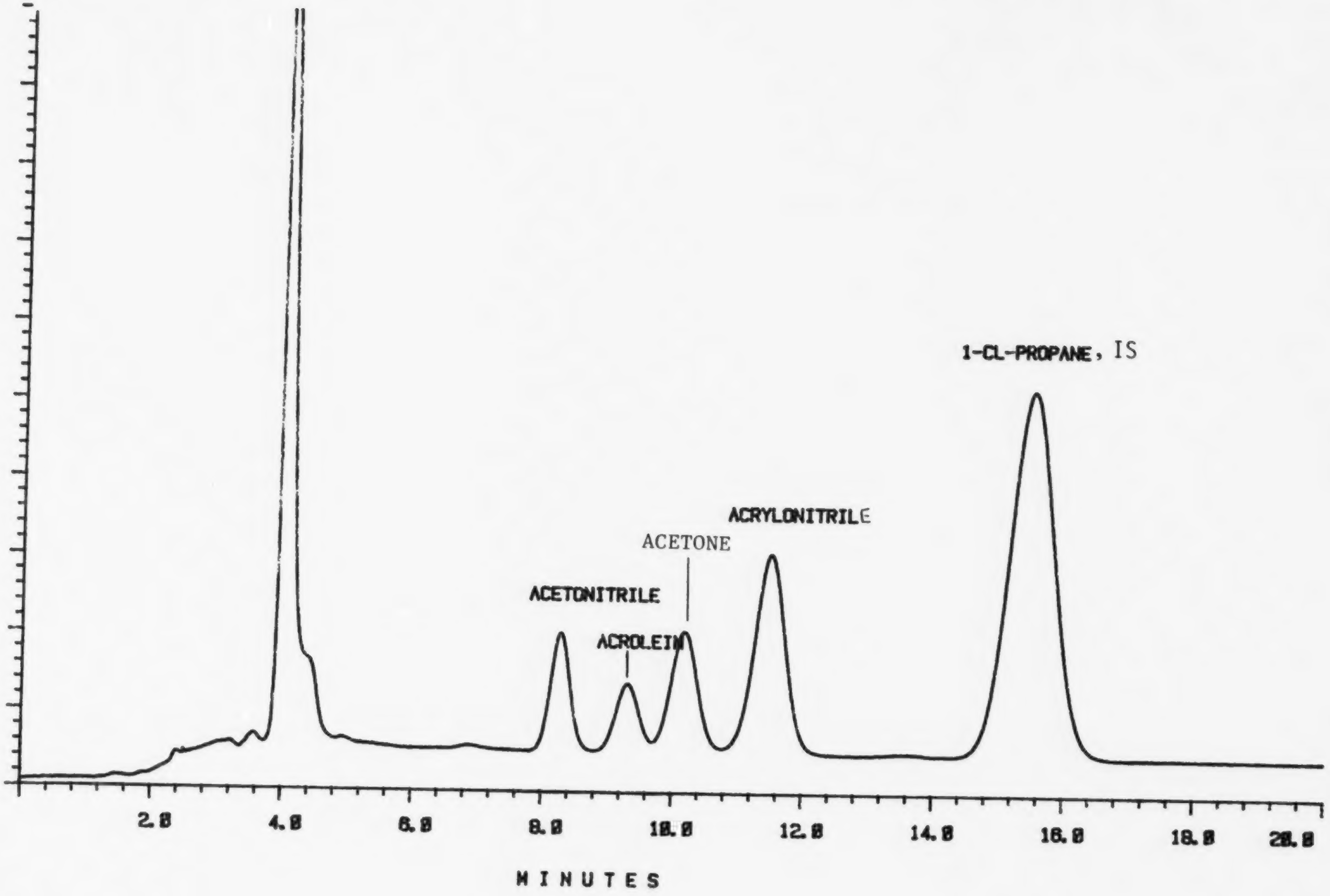


Figure 13. GC-FID chromatogram of low spike level groundwater analyzed using modified Method 8030 and Method 5030.

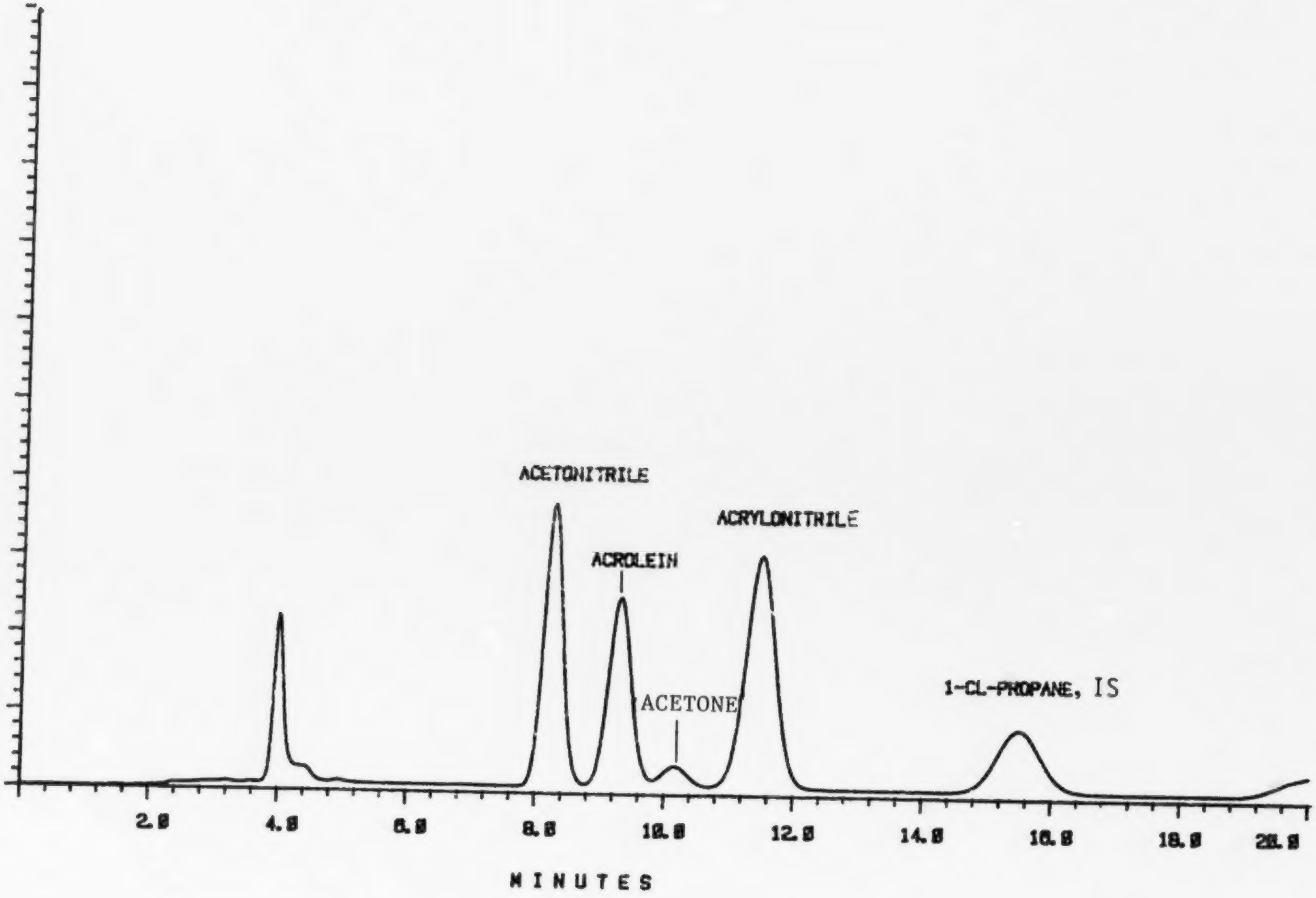


Figure 14. GC-FID chromatogram of high spike level groundwater analyzed using modified Method 8030 and Method 5030.

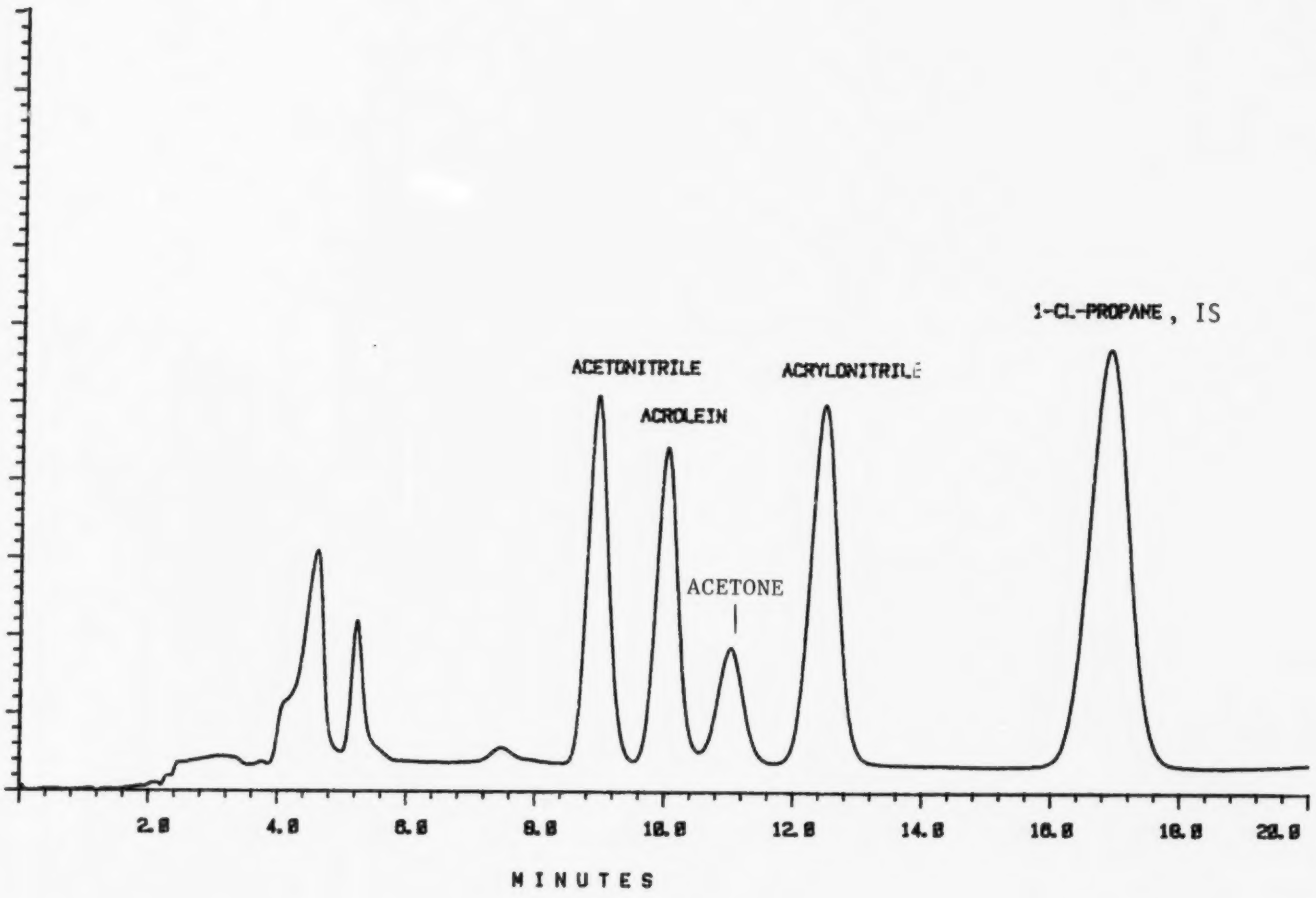


Figure 15. GC-FID chromatogram of a 10 µg/g calibration standard for 2-gm PEG extracts analyzed using modified Method 8030 and Method 5030.

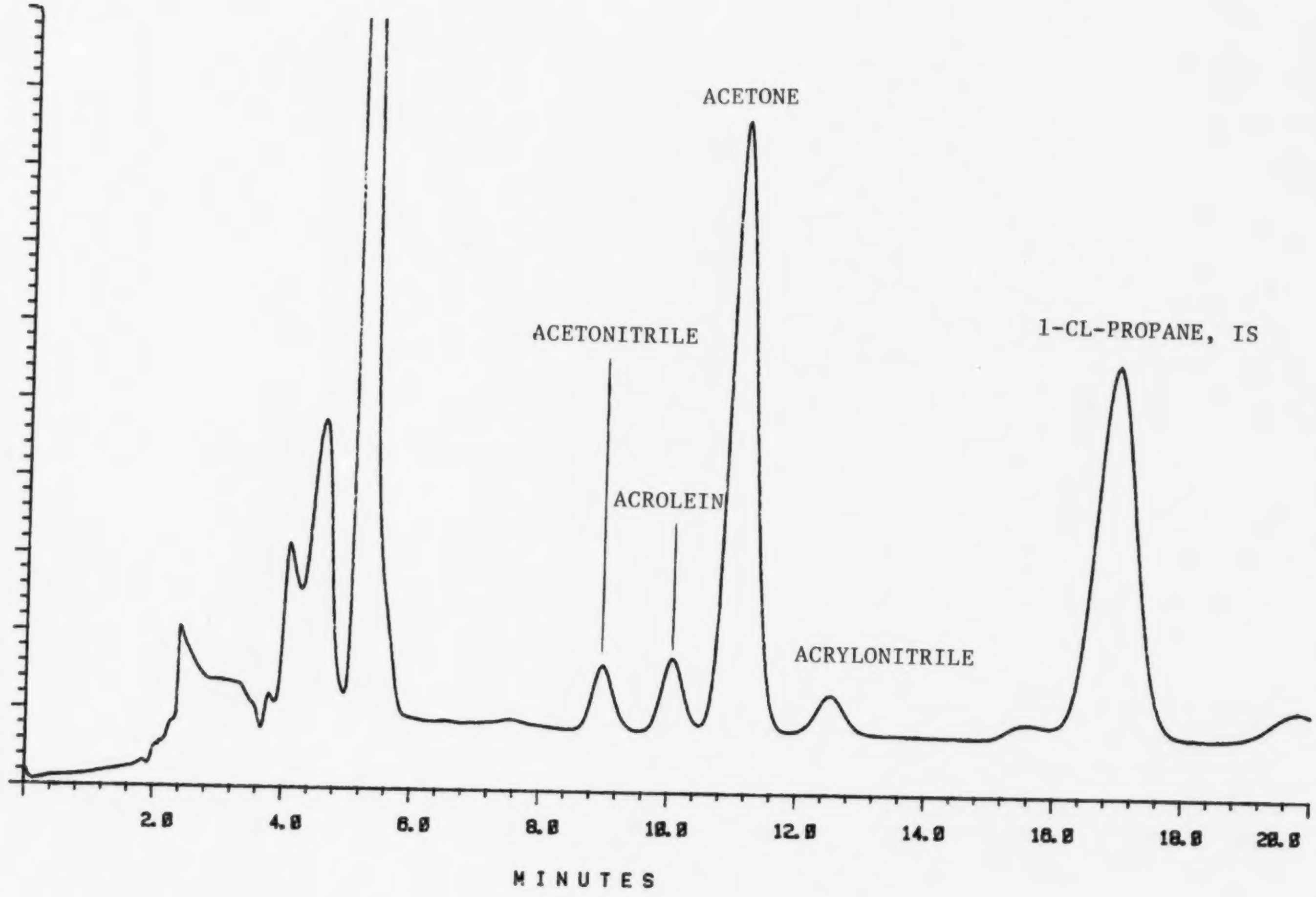


Figure 16. GC-FID chromatogram of spiked PEG for MDL determination analyzed using modified Method 8030 and Method 5030.

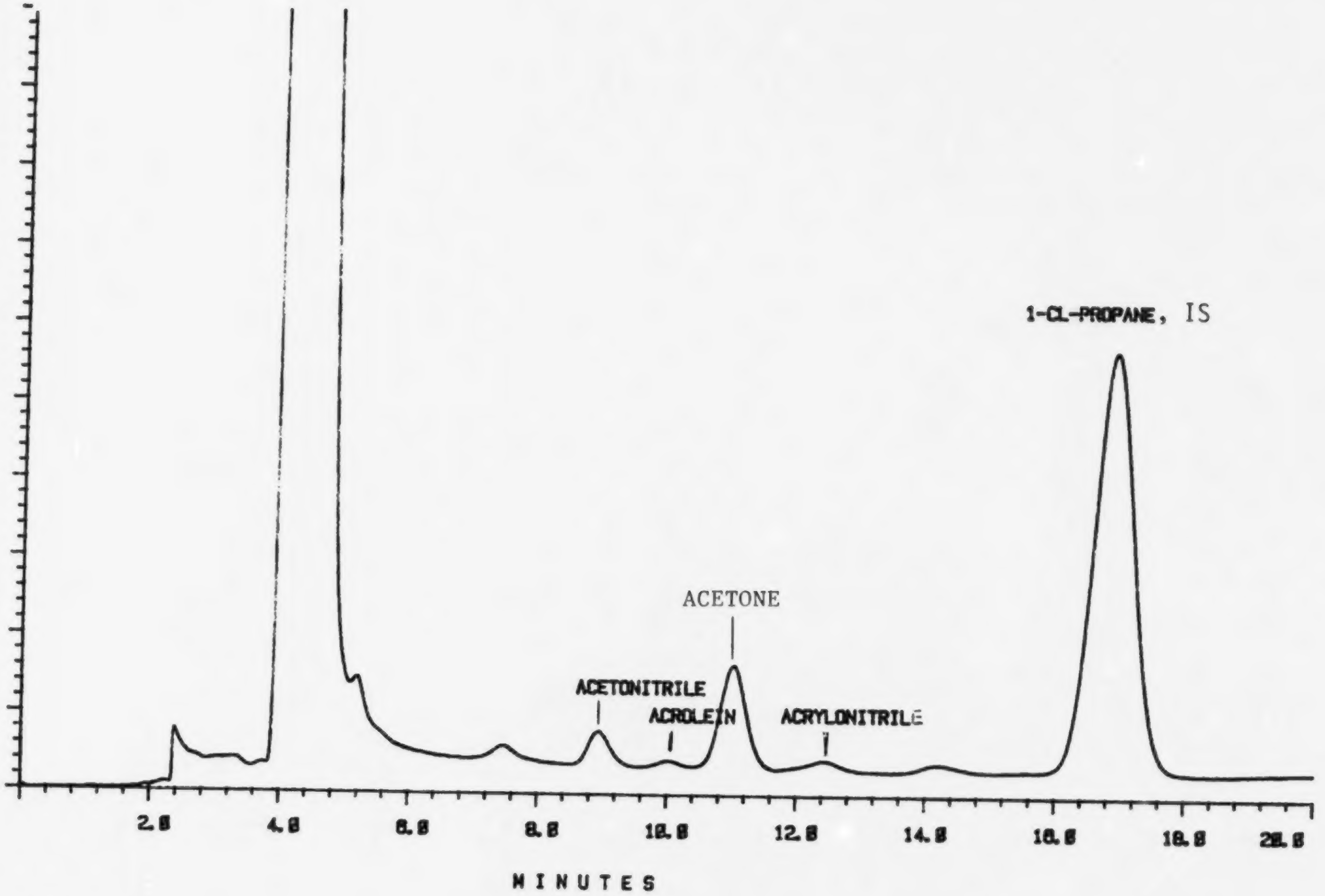


Figure 17. GC-FID chromatogram of PEG extract of unspiked solid waste analyzed using modified Method 8030 and Method 5030.

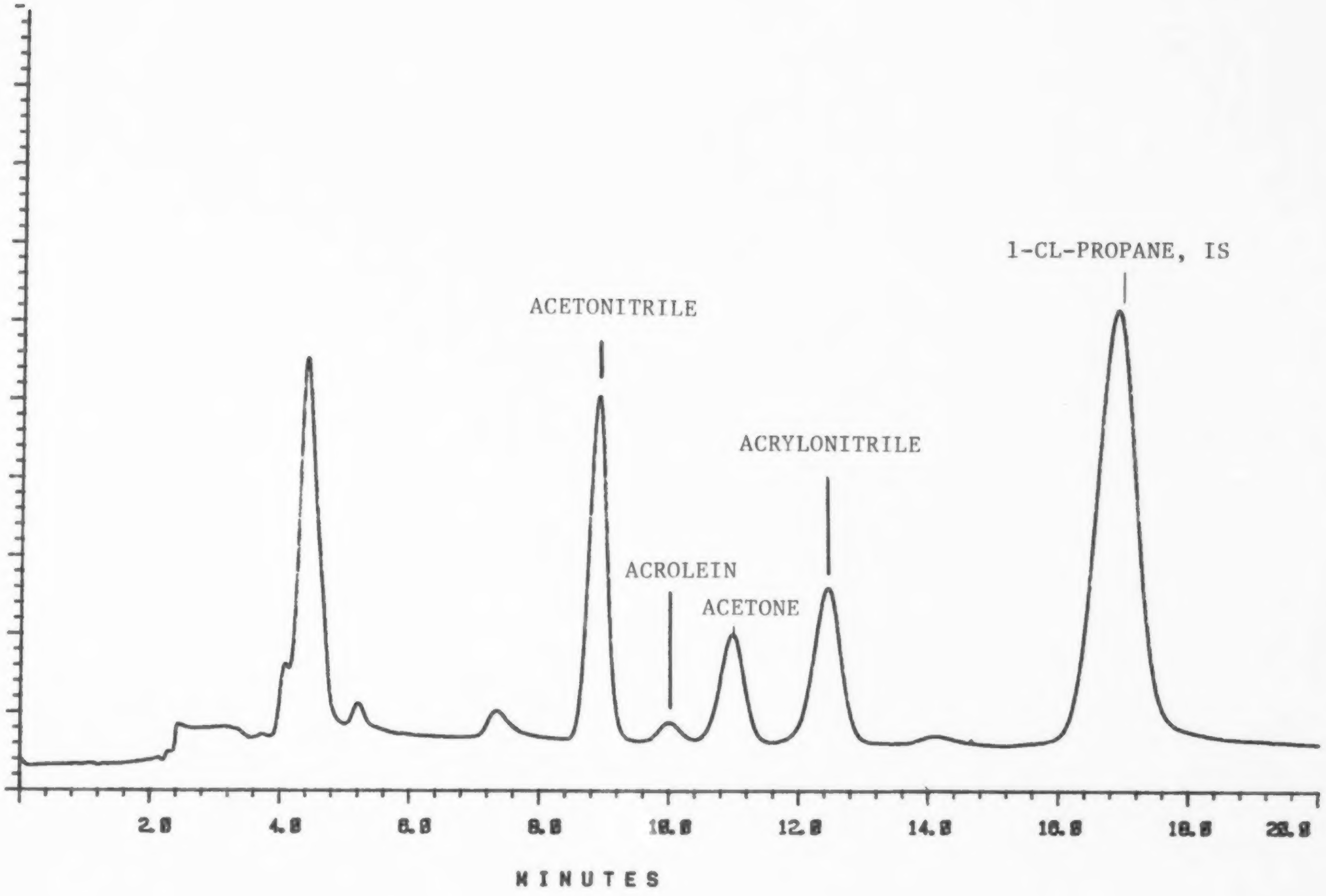


Figure 18. GC-FID chromatogram of PEG extract of low spike level solid waste analyzed using modified Method 8030 and Method 5030.

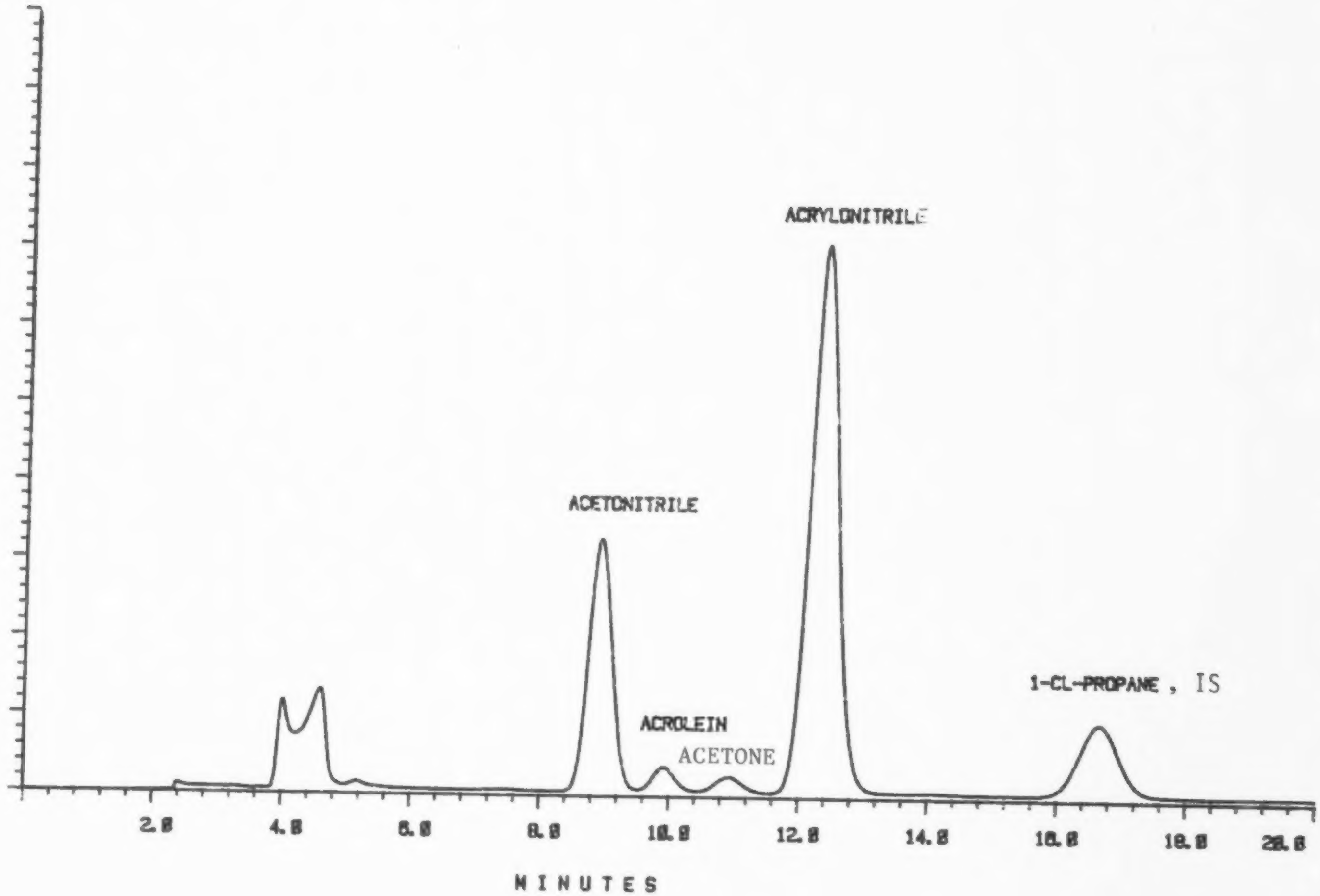


Figure 19. GC-FID chromatogram of PEG extract of high spike level solid waste analyzed using modified Method 8030 and Method 5030.

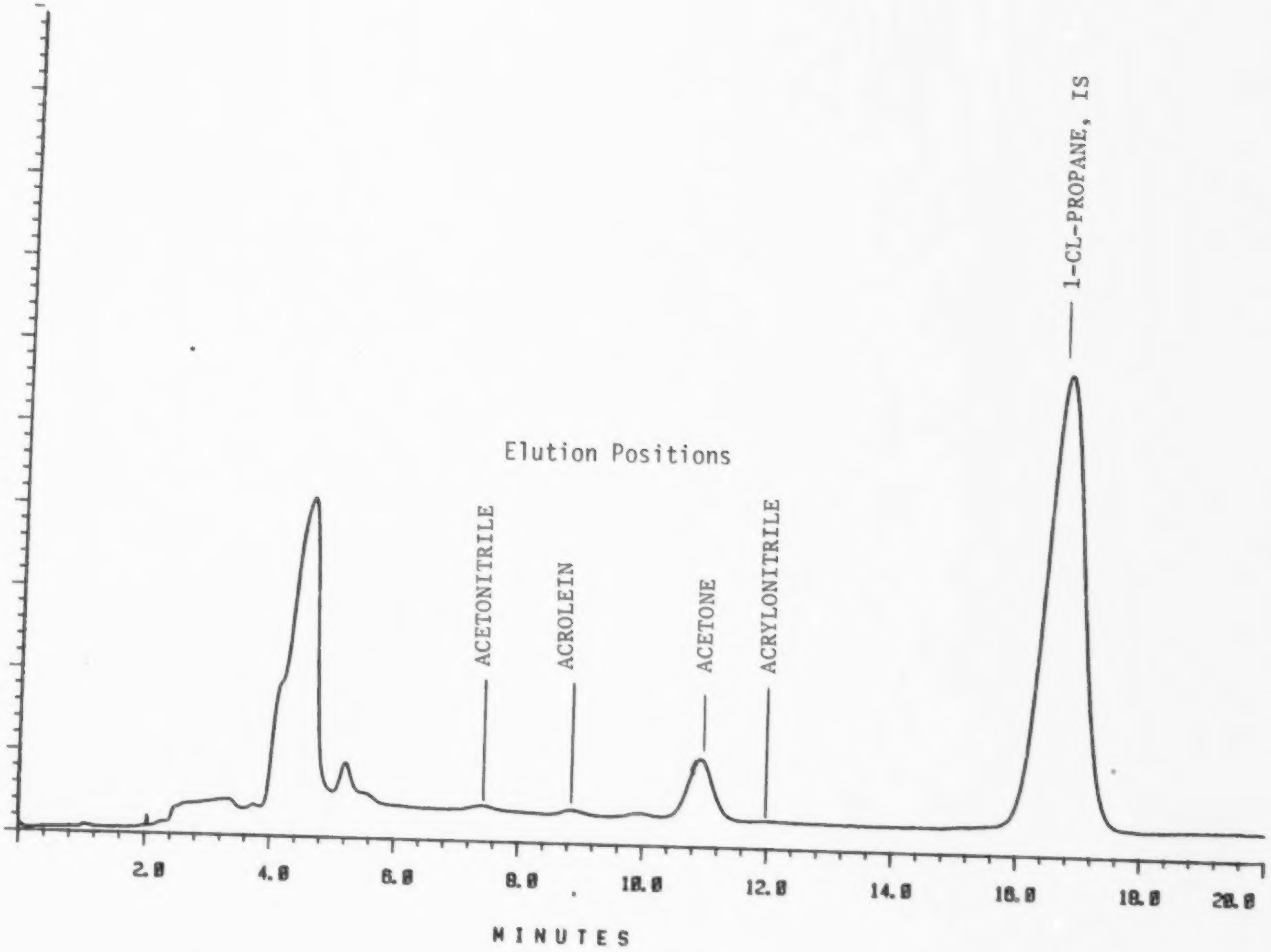


FIGURE 20. GC-FID chromatogram of blank PEG analyzed using modified Method 8030 and Method 5030.

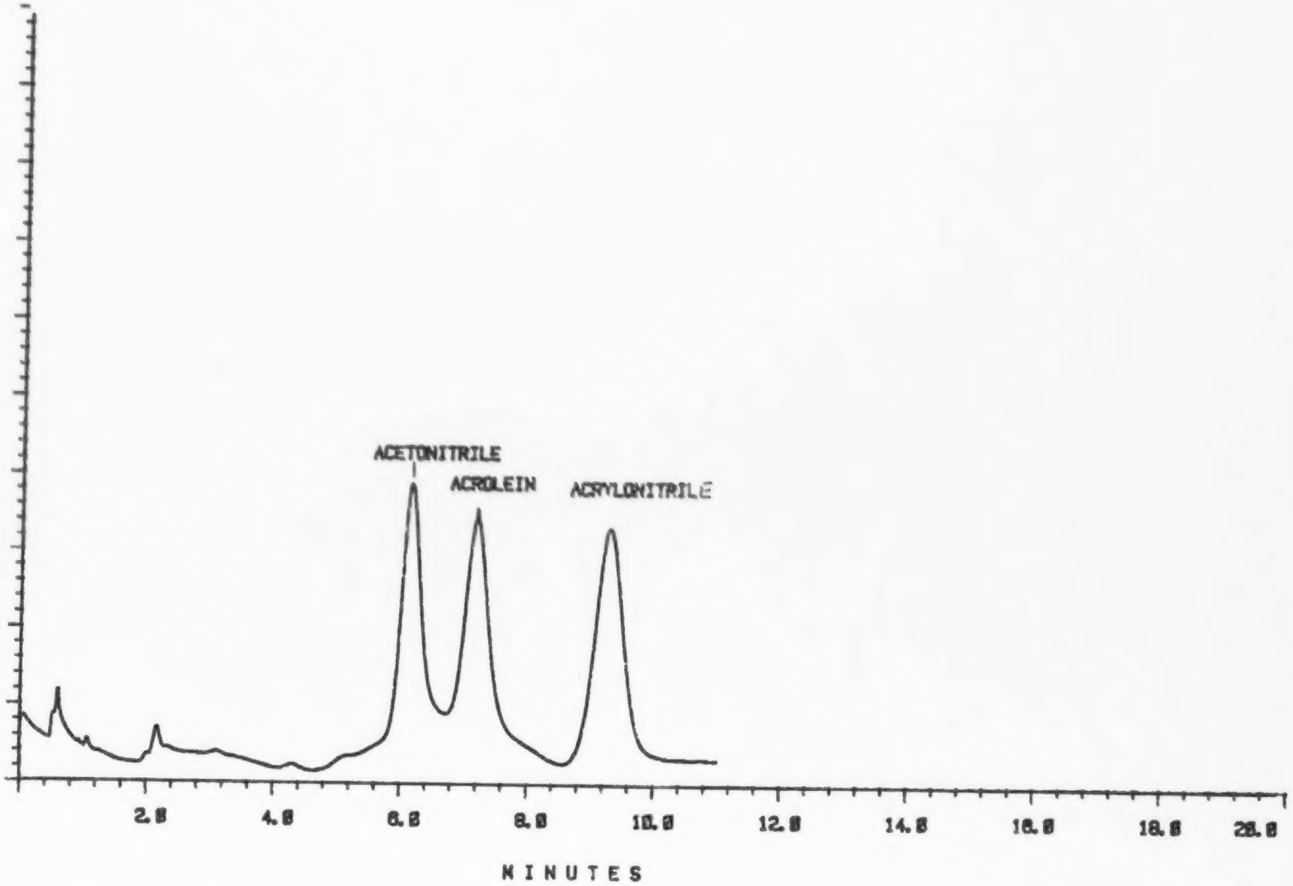


Figure 21. GC-FID chromatogram of 6.0 μg/mL calibration standard in toluene analyzed using modified Method 8030 with direct liquid injection of 5.0 μL.

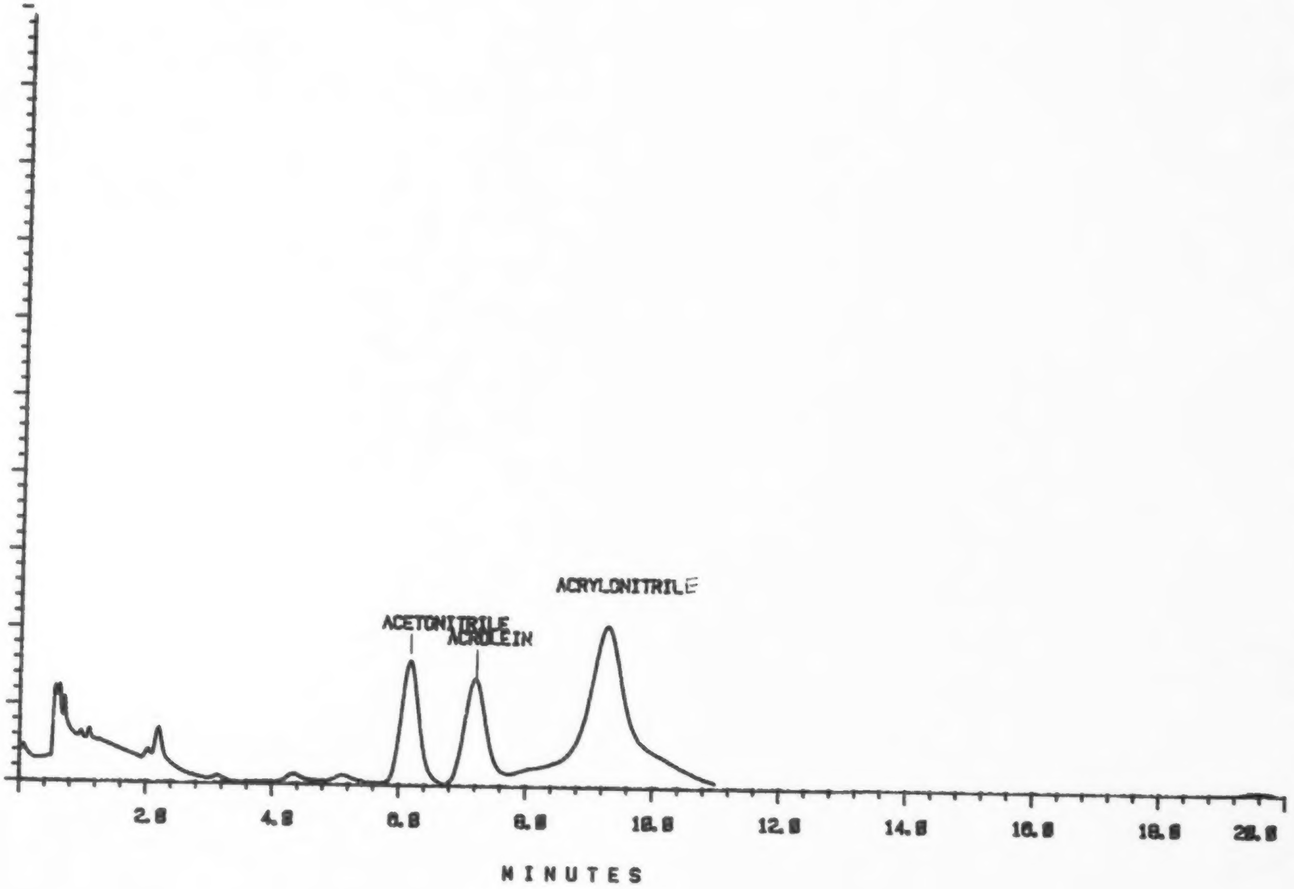


Figure 22. GC-FID chromatogram for MDL determination of a 3.0 µg/L sample in toluene analyzed using modified Method 8030 with direct liquid injection of 5.0 µL.

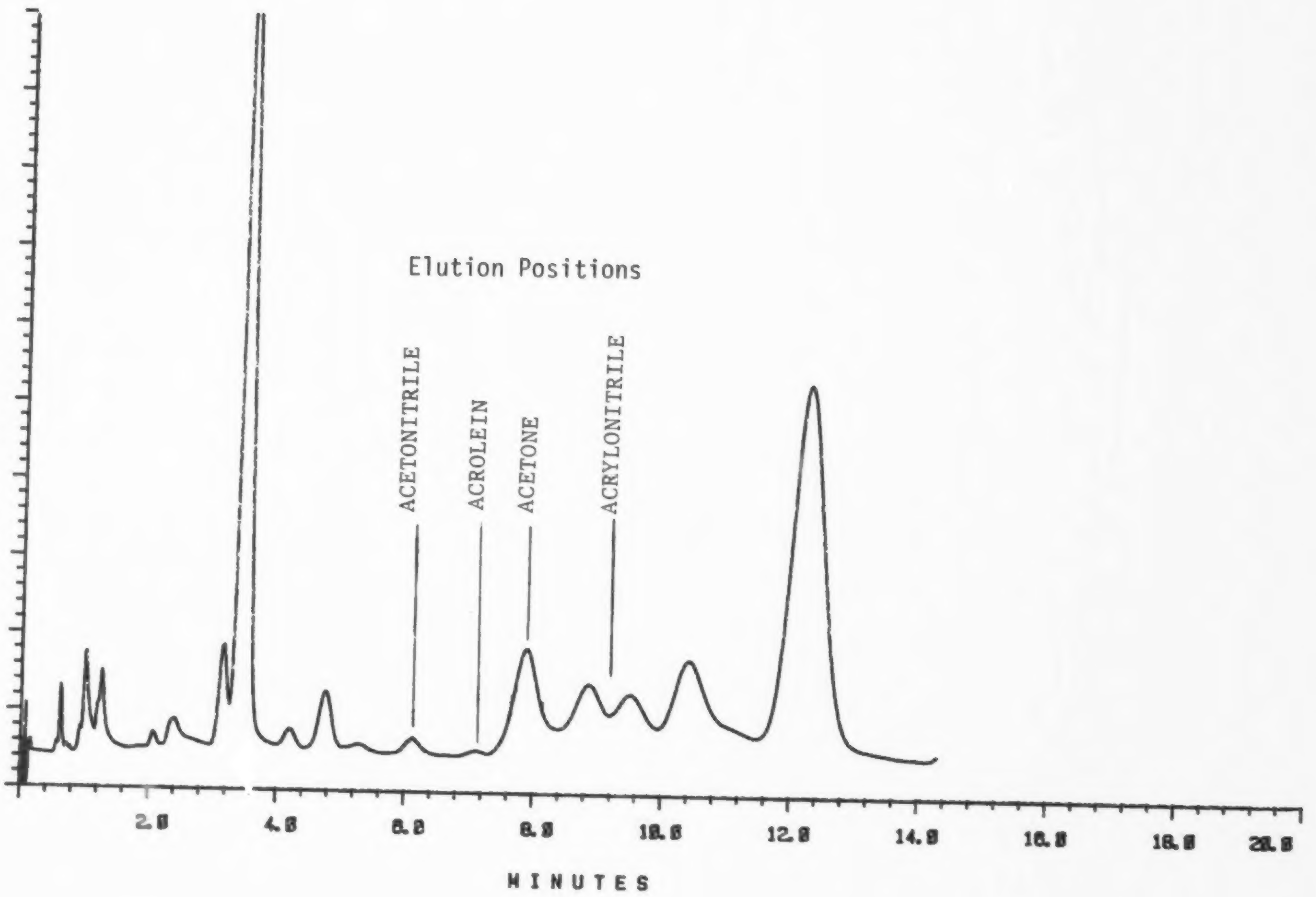


Figure 23. GC-FID chromatogram of unspiked liquid organic waste analyzed using modified Method 8030 with direct liquid injection of 5.0 µL.

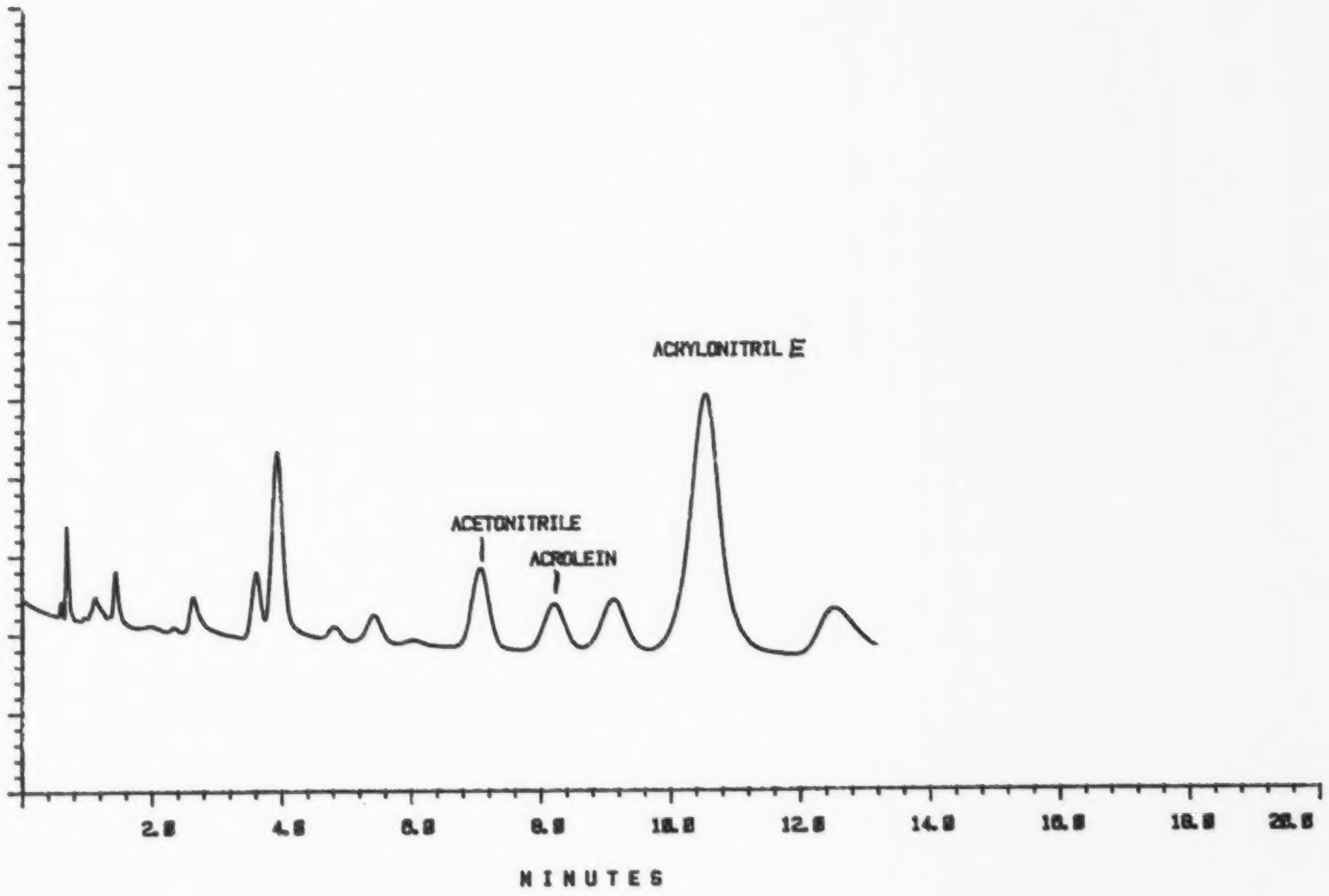


Figure 24. GC-FID chromatogram of low spike level liquid organic waste analyzed using modified Method 8030 with direct liquid injection of 5.0 μL.

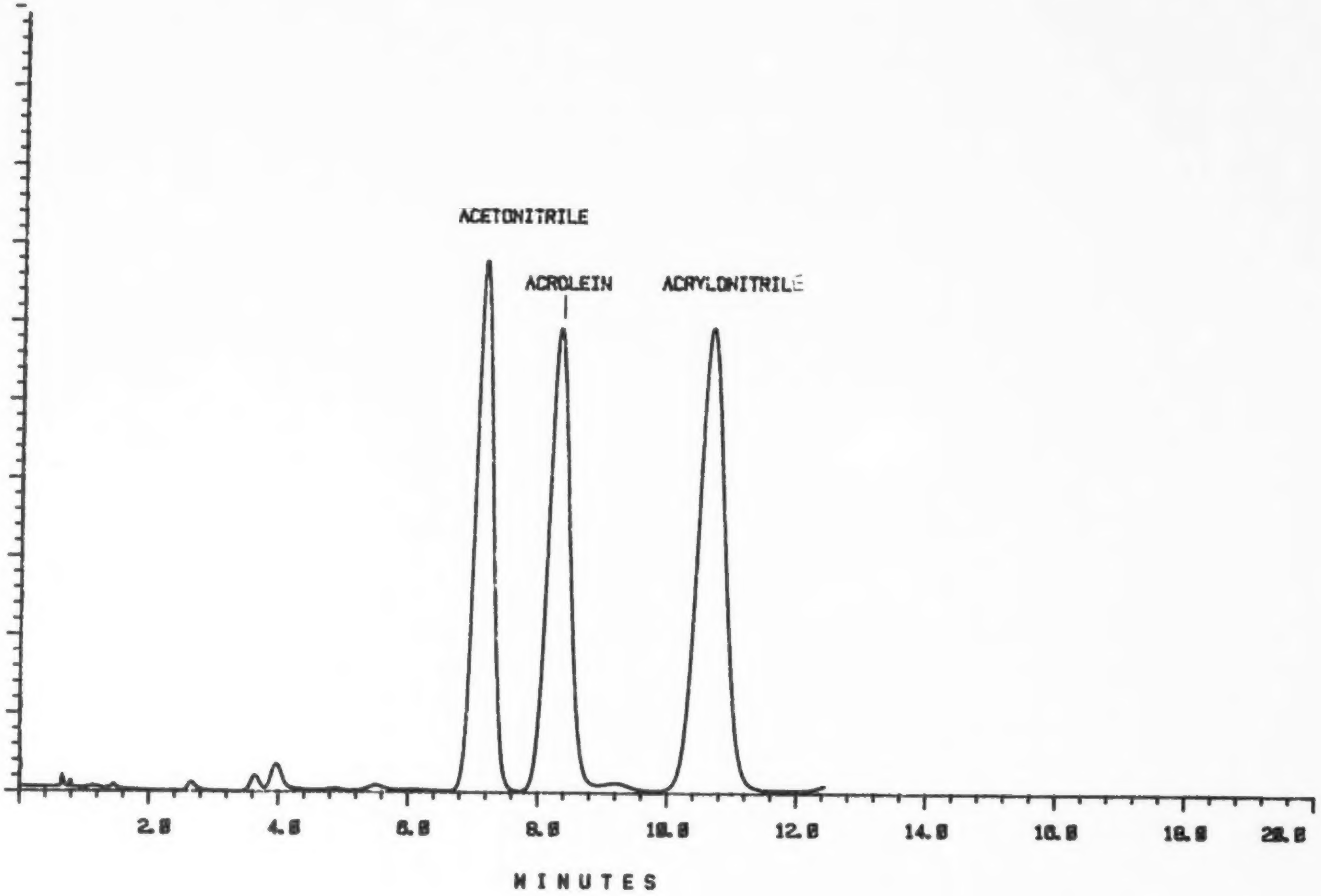


Figure 25. GC-FID chromatogram of high spike level liquid organic waste analyzed using modified Method 8030 with direct liquid injection of 5.0 μL.

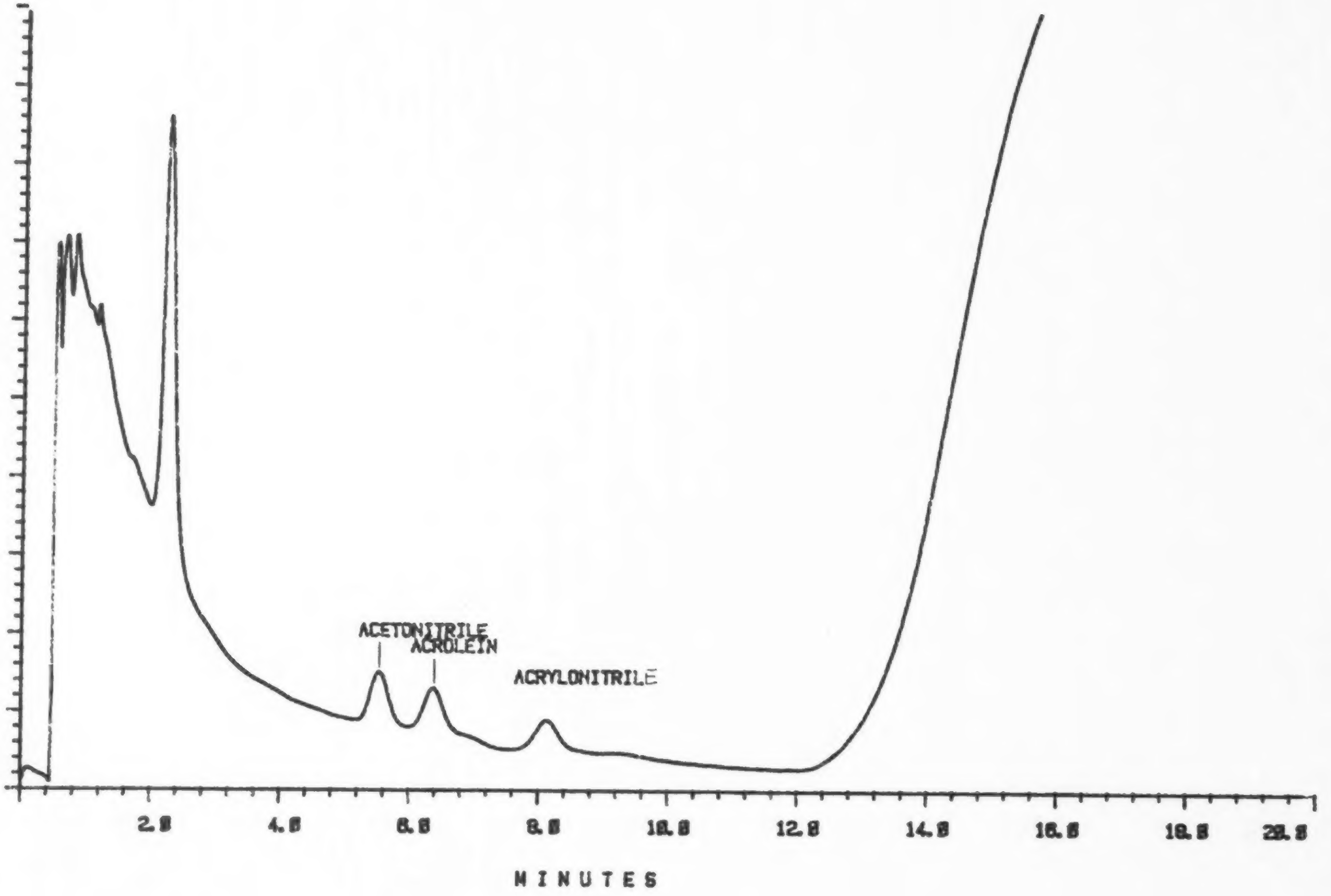


Figure 26. GC-FID chromatogram of reagent water spiked at 1.0 mg/L for MDL determination using modified Method 8030 and Method 5020 (no standard addition).

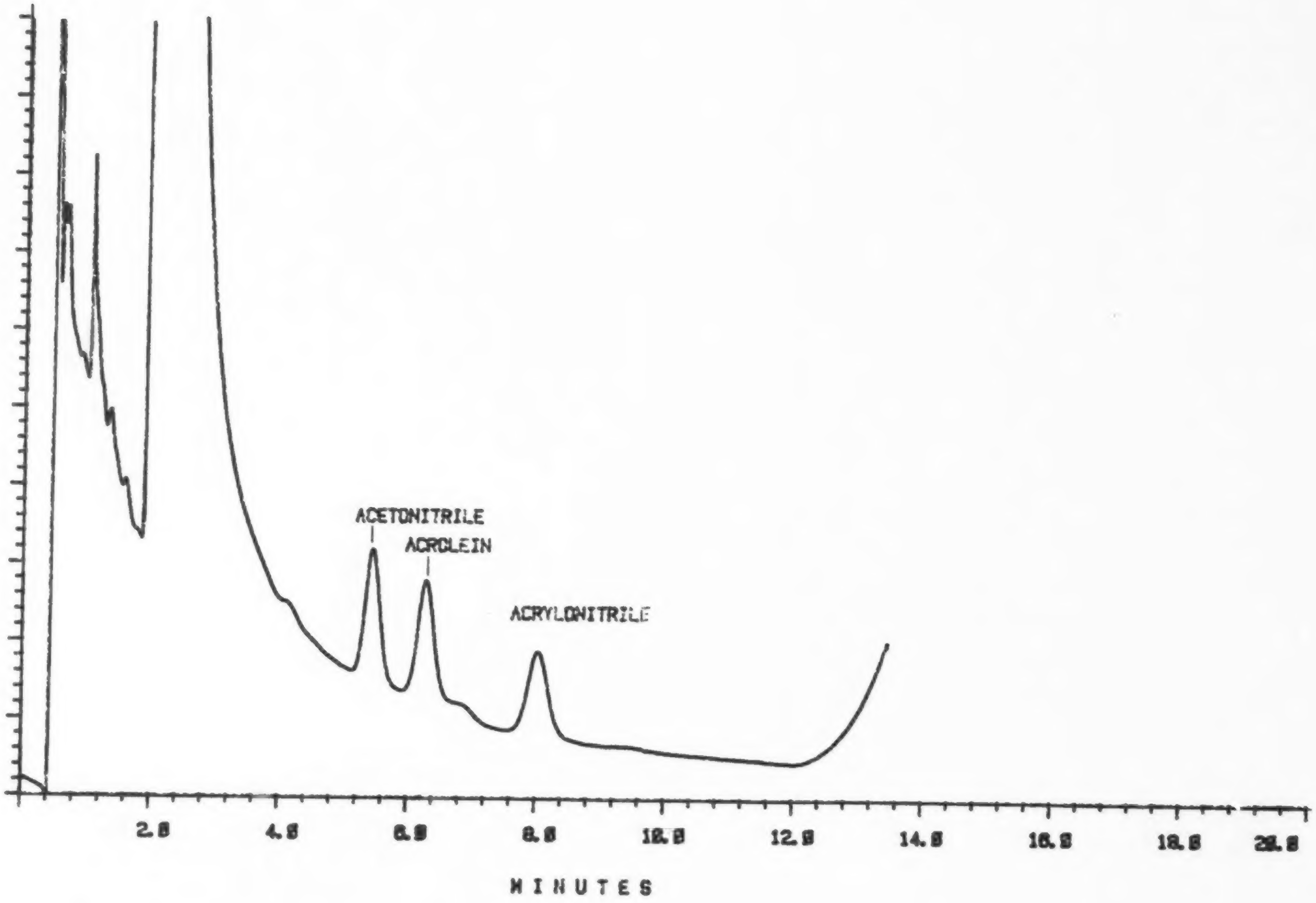


Figure 27. GC-FID chromatogram of reagent water spiked at 1.0 mg/L for MDL determination using modified Method 8030 and Method 5020 (with standard addition).

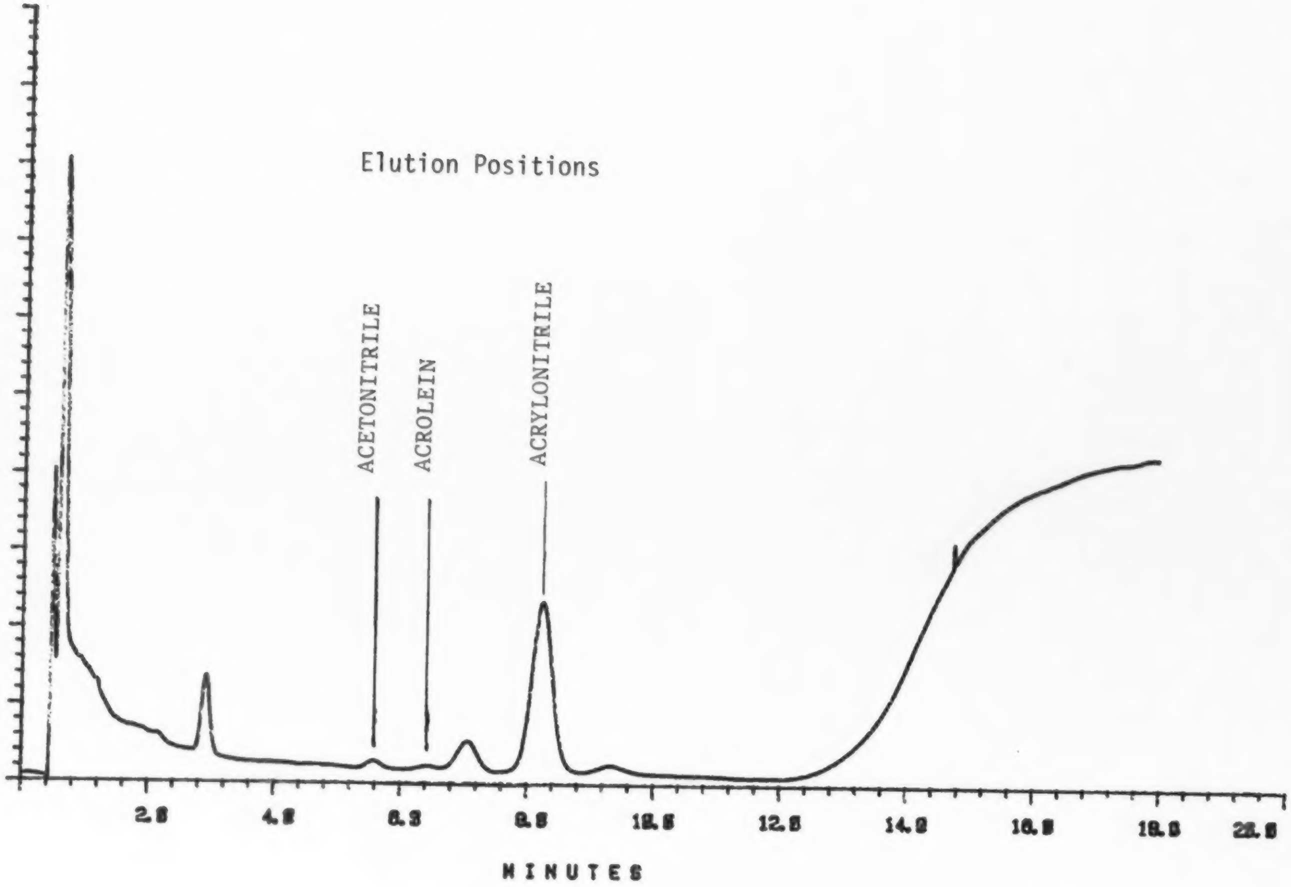


Figure 28. GC-FID chromatogram of unspiked solid waste using modified Method 8030 and Method 5020 (no standard addition).

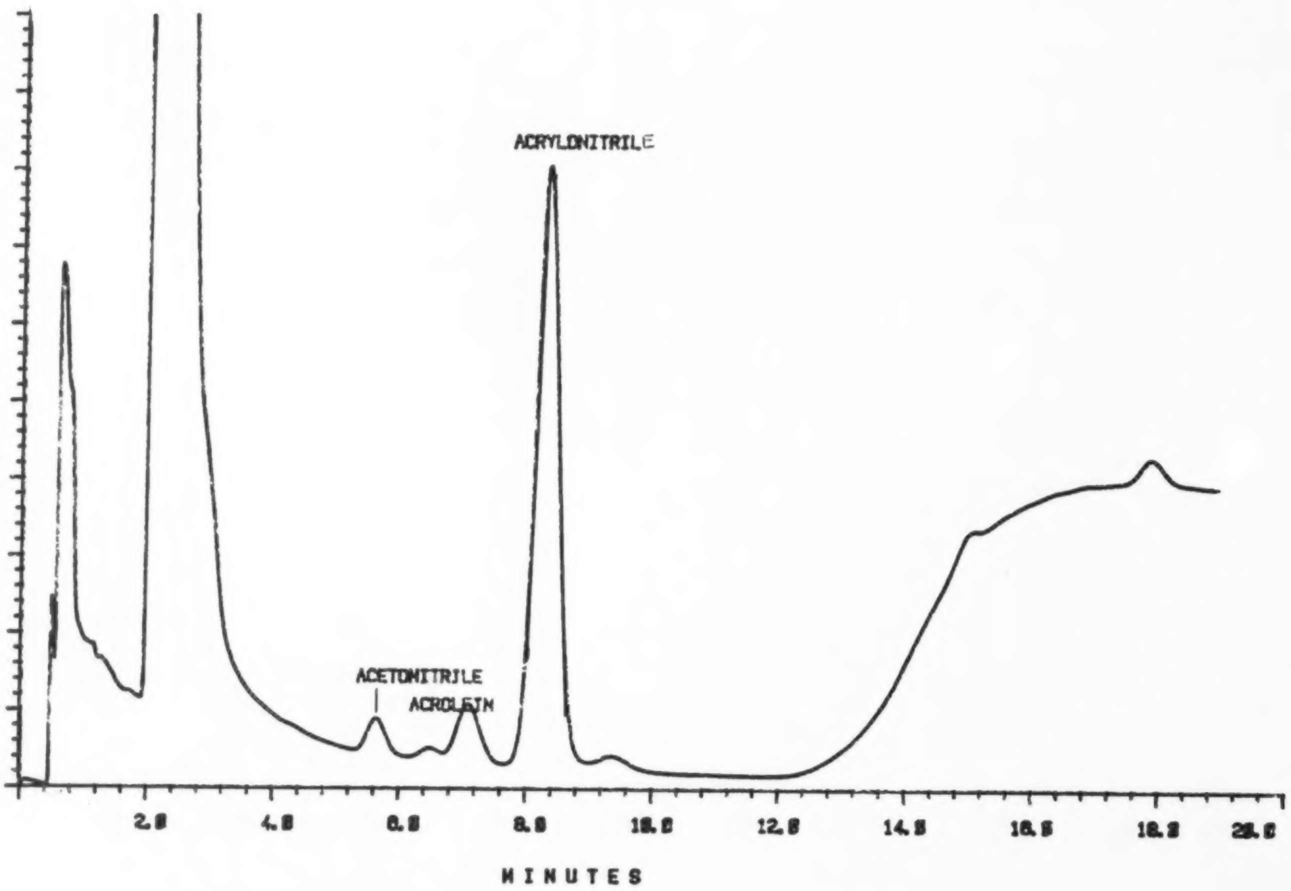


Figure 29. GC-FID chromatogram of unspiked solid waste using modified Method 8030 and Method 5020 (with standard addition).

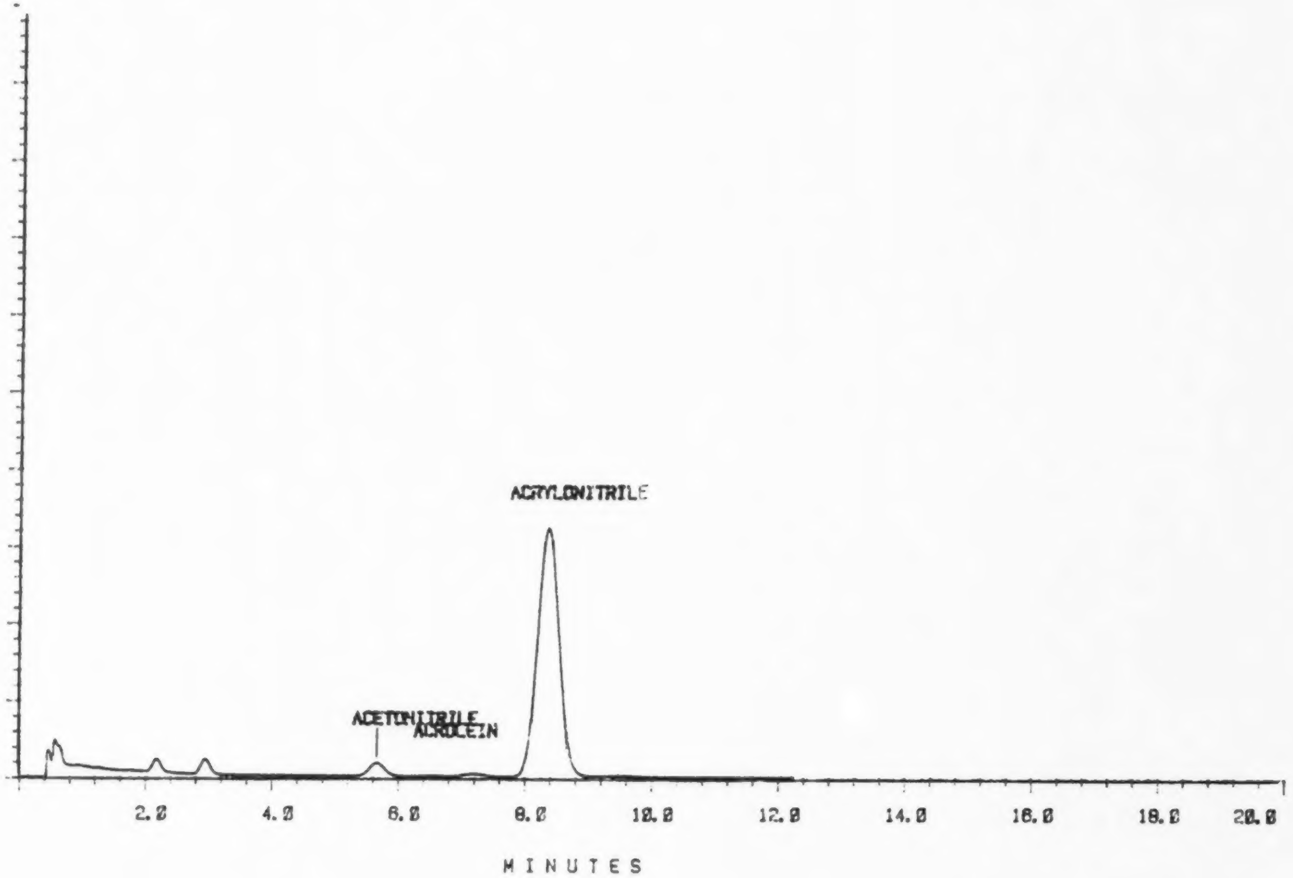


Figure 30. GC-FID chromatogram of low spike level solid waste using modified Method 8030 and Method 5020 (no standard addition).

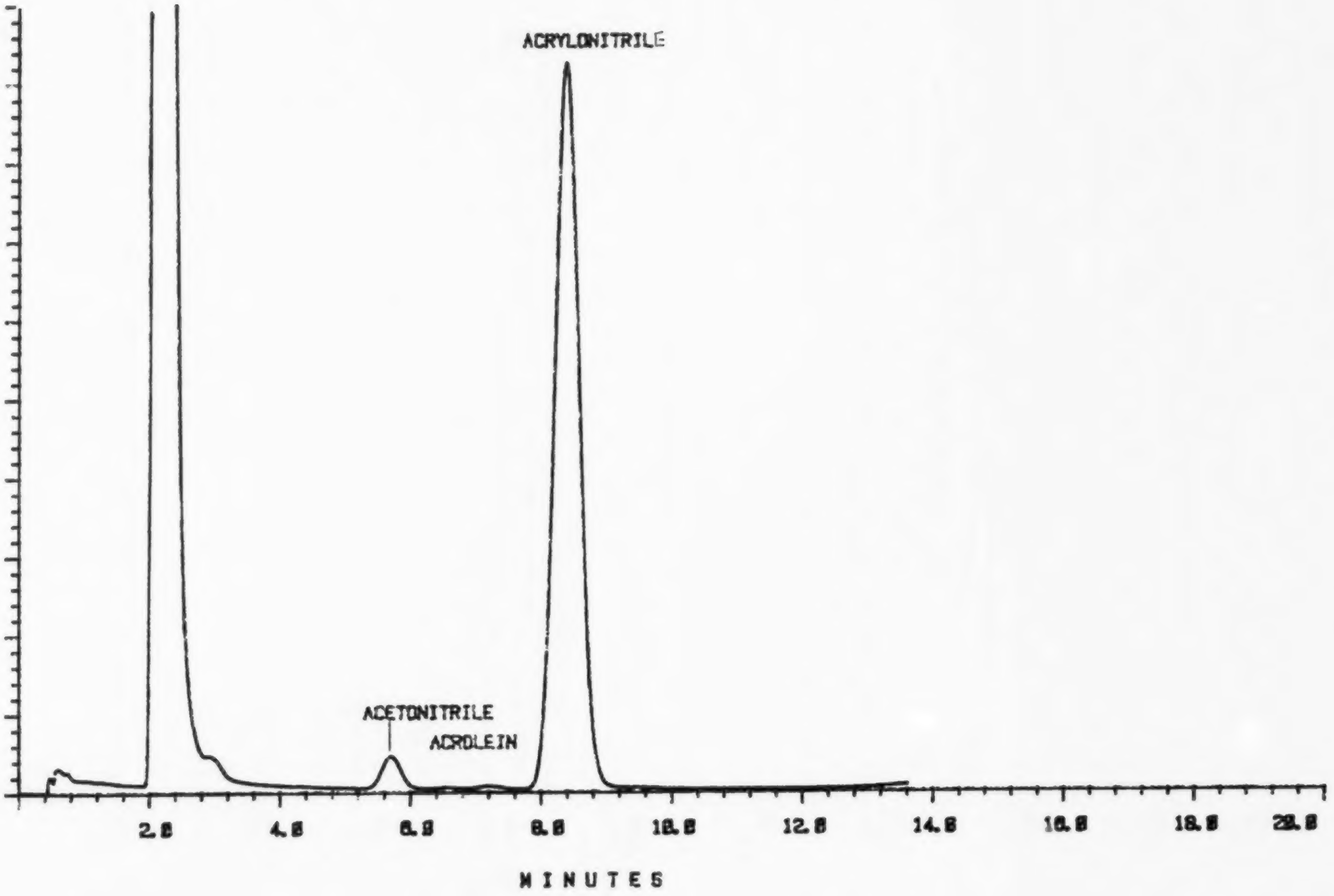


Figure 31. GC-FID chromatogram of low spike level solid waste using modified Method 8030 and Method 5020 (with standard addition).

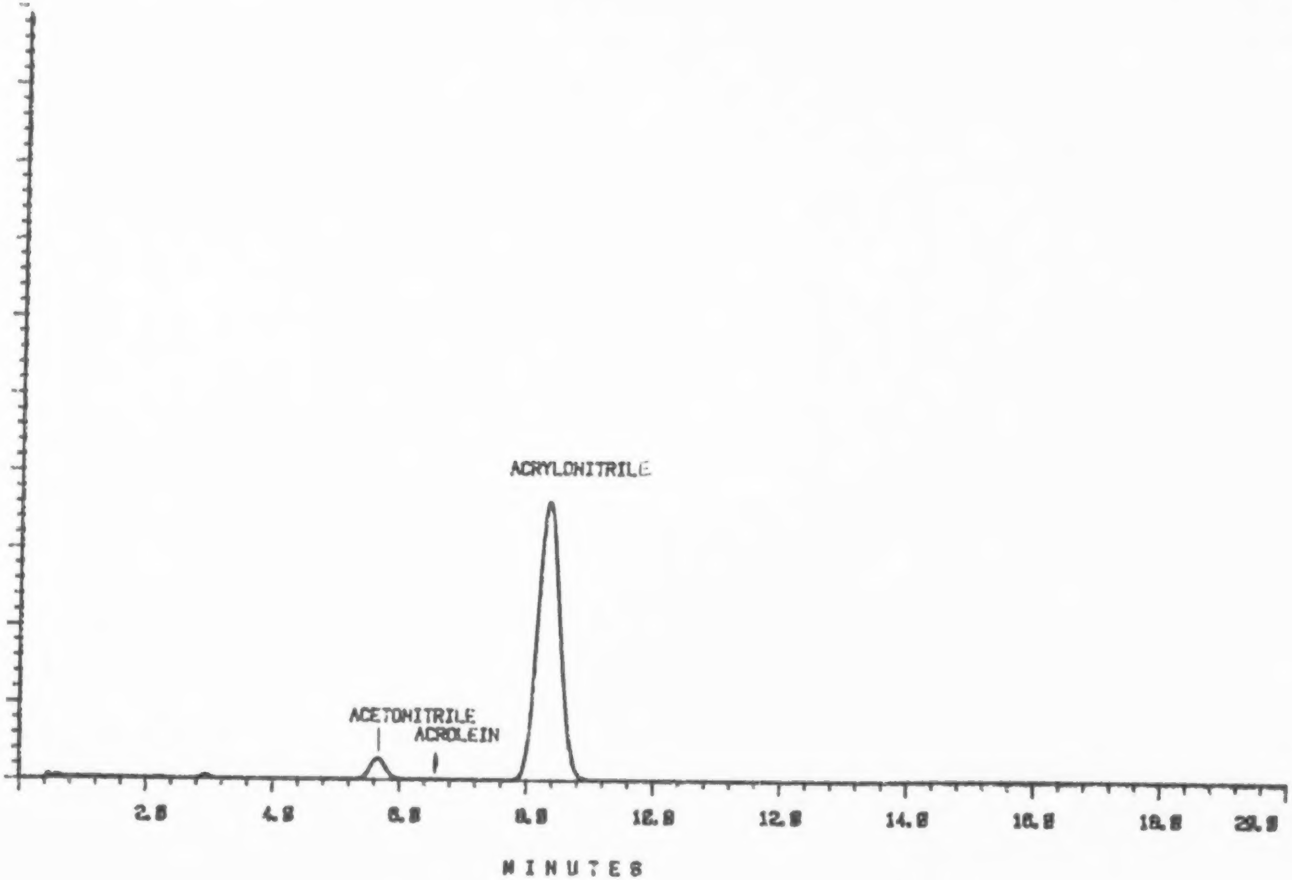


Figure 32. GC-FID chromatogram of high spike level solid waste using modified Method 8030 and Method 5020 (no standard addition).

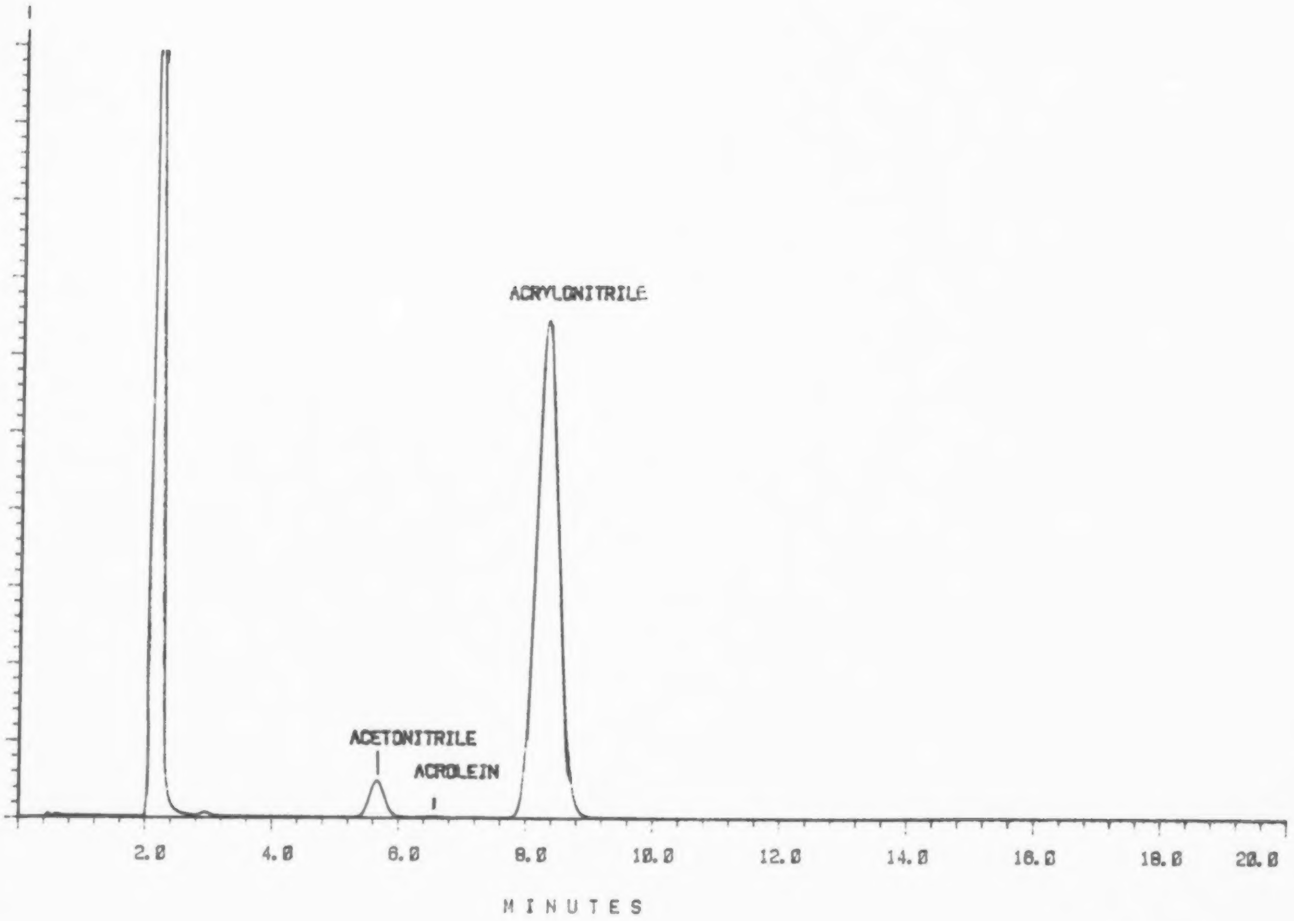


Figure 33. GC-FID chromatogram of high spike level solid waste using modified Method 8030 and Method 5020 (with standard addition).

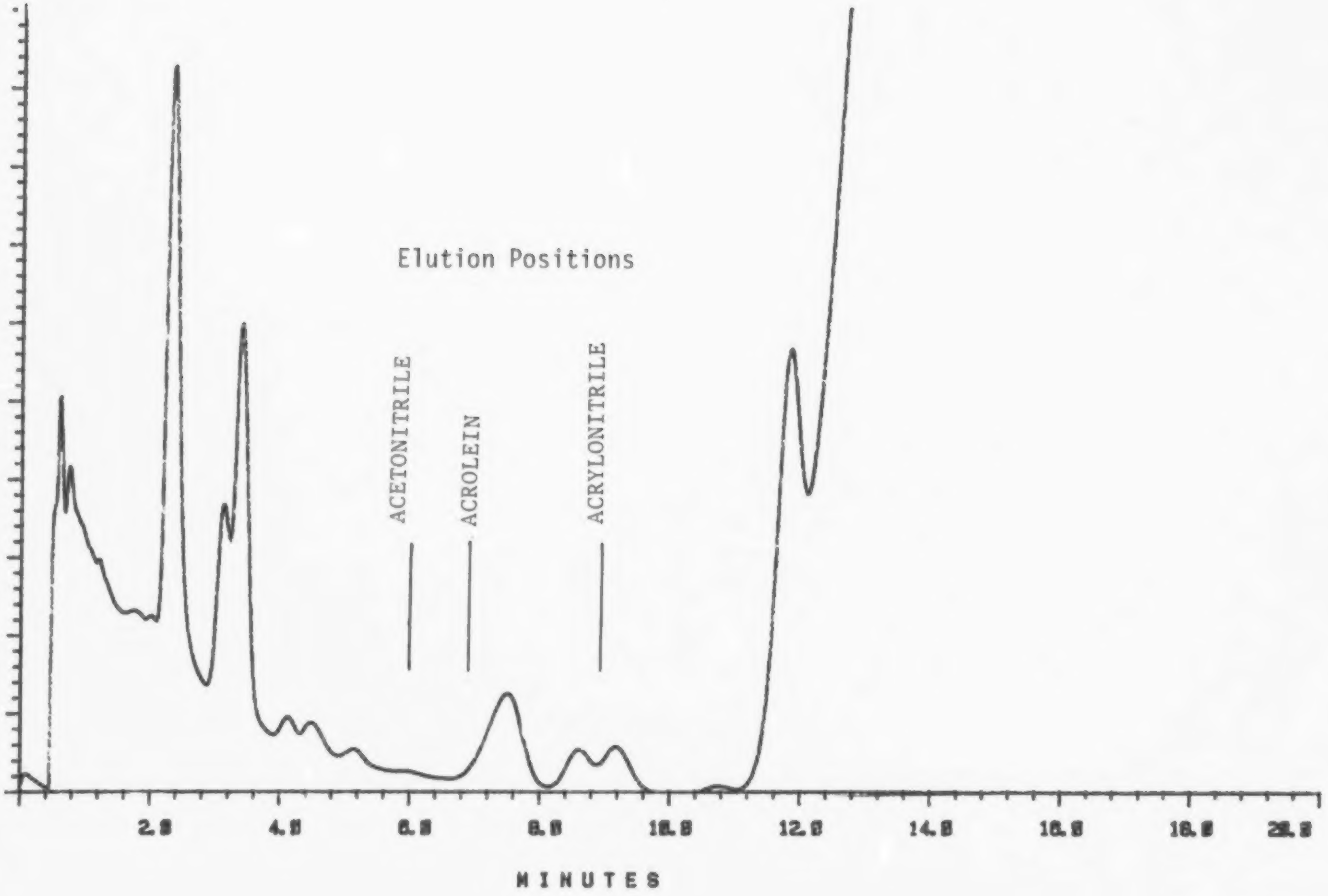


Figure 34. GC-FID chromatogram of unspiked liquid organic waste using modified Method 8030 and Method 5020 (no standard addition).

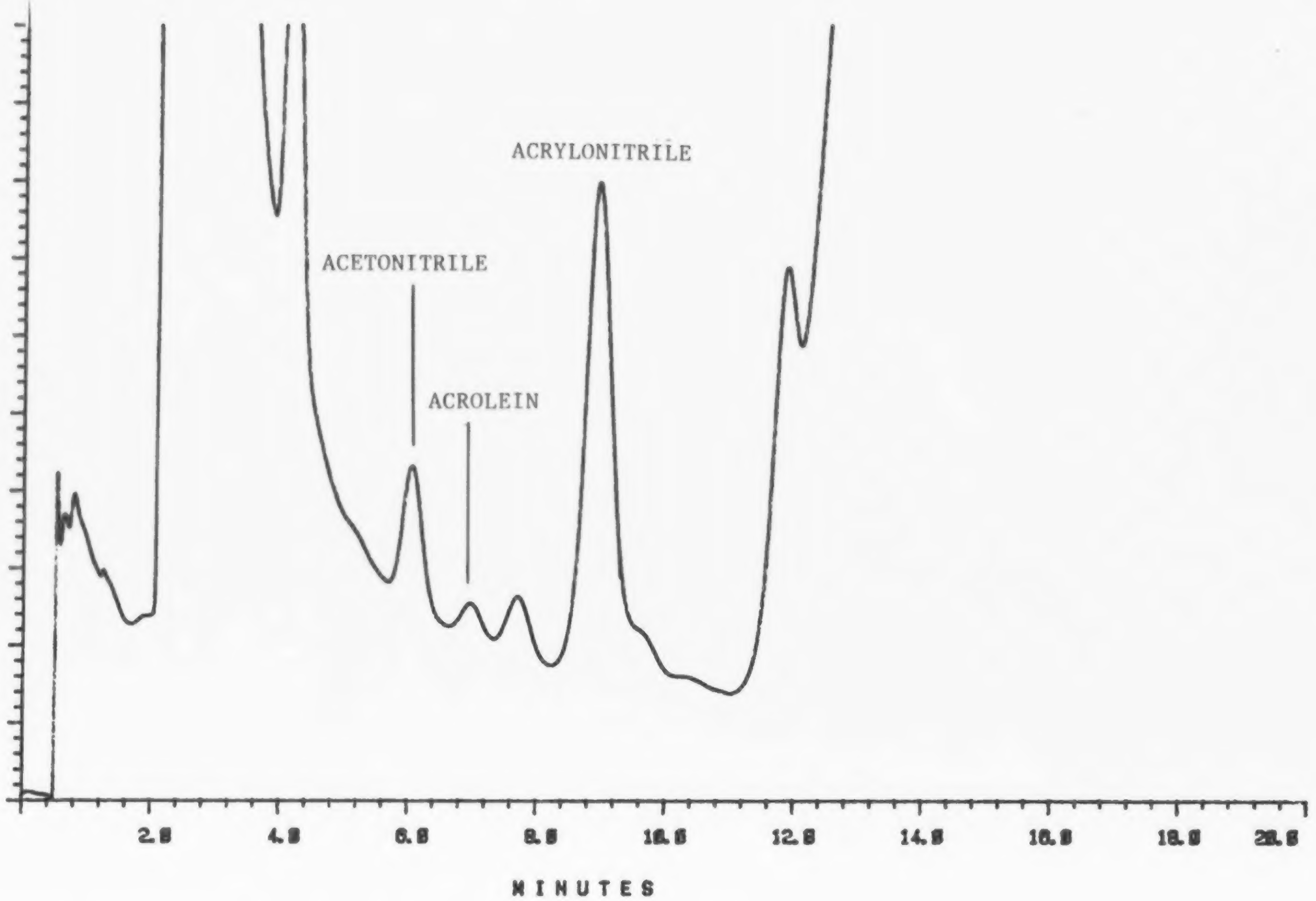


Figure 35. GC-FID chromatogram of unspiked liquid organic waste using modified Method 8030 and Method 5020 (with standard addition).

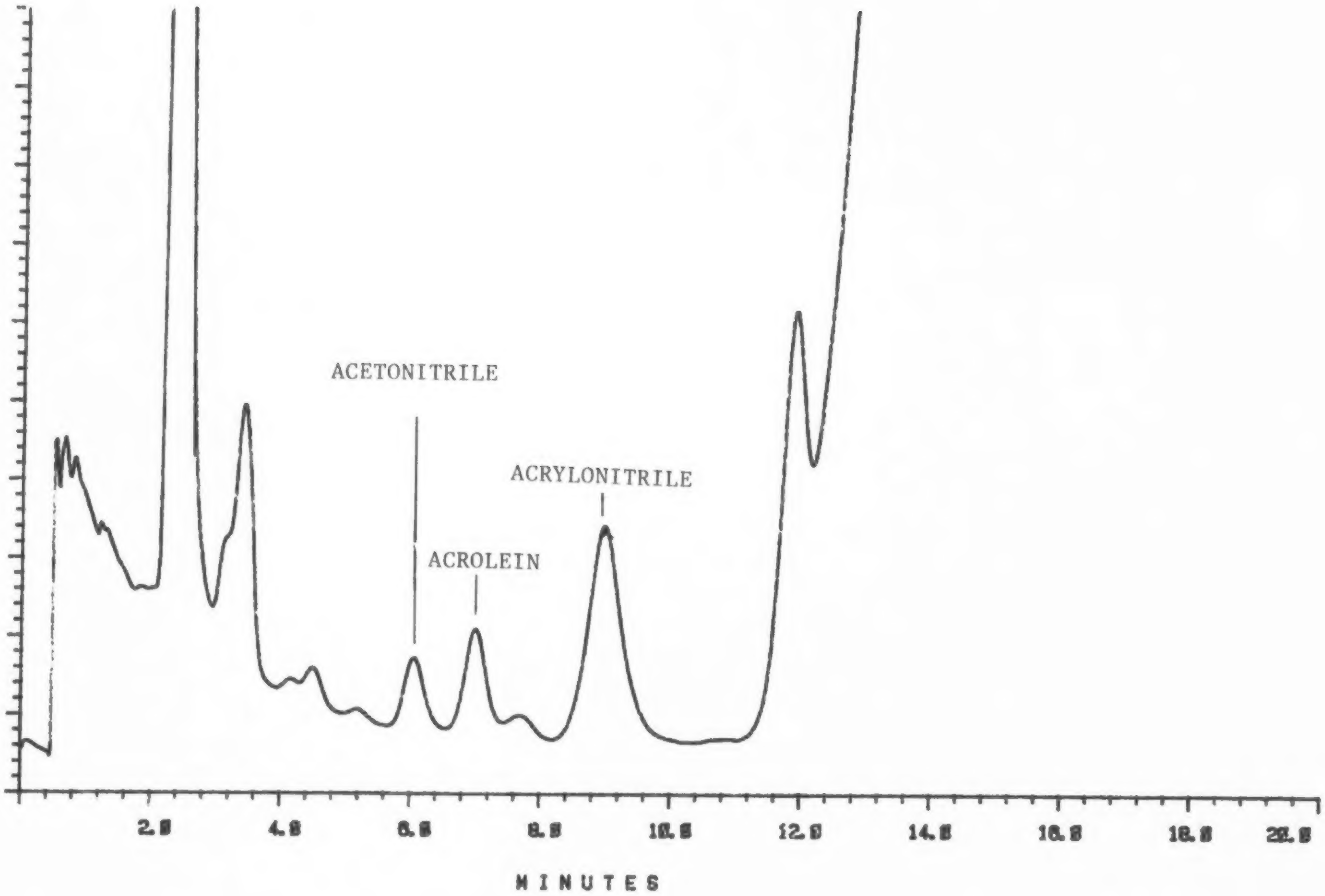


Figure 36. GC-FID chromatogram of low spike level liquid organic waste using modified Method 8030 and Method 5020 (no standard addition).

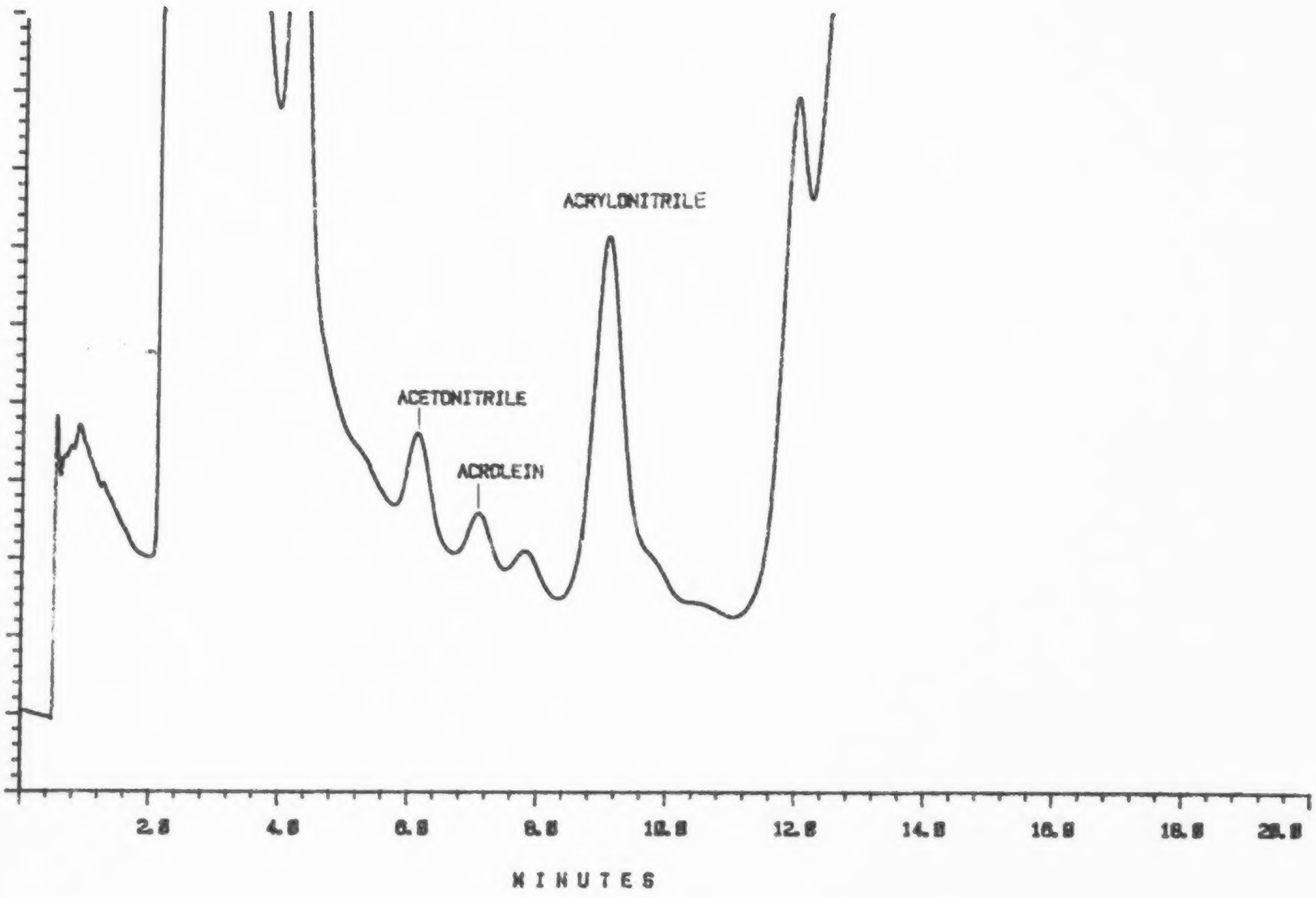


Figure 37. GC-FID chromatogram of low spike level liquid organic waste using modified Method 8030 and Method 5020 (with standard addition).

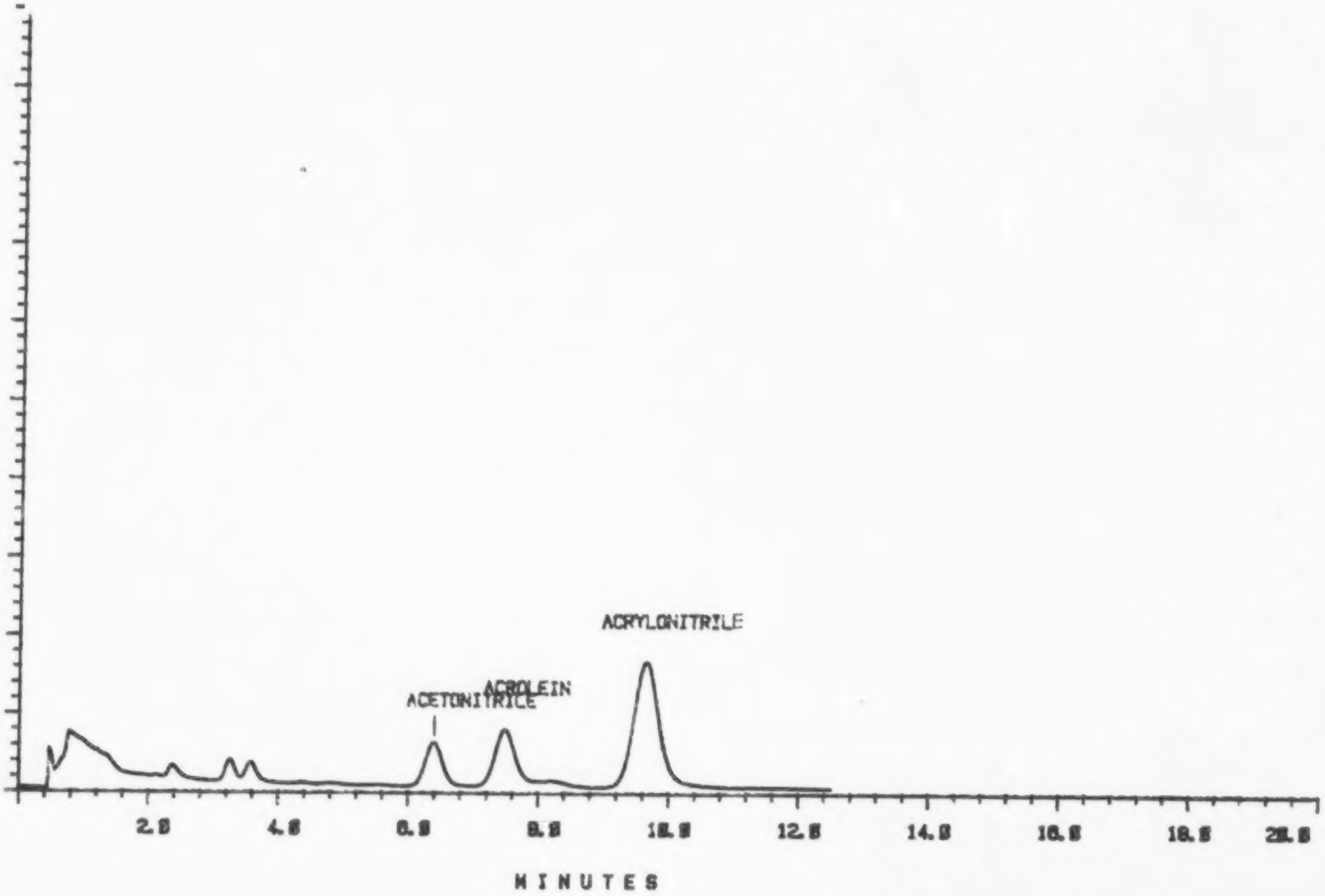


Figure 38. GC-FID chromatogram of high spike level liquid organic waste using modified Method 8030 and Method 5020 (no standard addition).

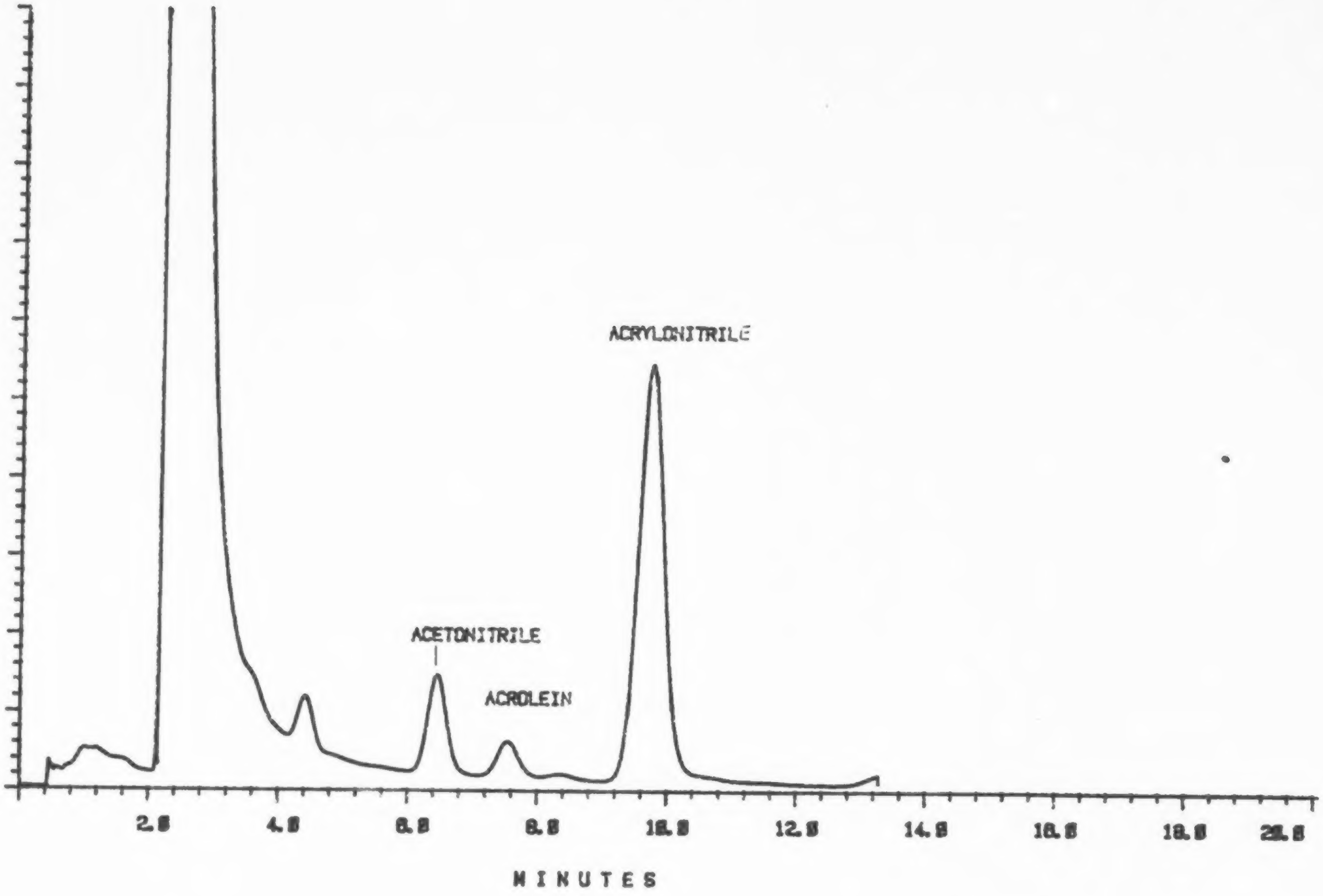


Figure 39. GC-FID chromatogram of high spike level liquid organic waste using modified Method 8030 and Method 5020 (with standard addition).

TABLE 2. GC PEAK AREAS FOR THE DETERMINATION OF THE LINEAR DYNAMIC RANGE OF THE DETECTOR--EXTERNAL STANDARD METHOD

		Average GC Peak Area(a) Obtained from 2 µl Injections for the Given Concentration, mg/l								
Compound	Statistical Parameter	0.5(b)	1.0(b)	2.0(b)	4.0(c)	15.0(c)	50(c)	100(b)	250(b)	500(b)
Acetonitrile	Mean	1.39(a)	3.03	6.60	15.7	59	193	456	1200	2370
	Standard Deviation	±0.13	±0.64	±0.09	±2.8	±11	±32	±18	±35	±80
	Relative Standard Deviation, %	9	21	1.3	18	19	16	3.9	2.9	3.4
Acrolein	Mean	2.39	4.17	8.63	19.9	71	225	524	1350	2800
	Standard Deviation	±0.29	±0.58	±0.46	±4.0	±12	±36	±22	±42	±90
	Relative Standard Deviation, %	12	14	5.4	20	18	16	4.2	3.1	3.1
Acrylonitrile	Mean	1.83	3.84	9.03	21.7	84	277	668	1710	3440
	Standard Deviation	±0.32	±0.70	±0.44	±4.7	±18	±55	±31	±50	±110
	Relative Standard Deviation, %	17	18	4.9	22	22	20	4.6	2.9	3.1

(a) Arbitrary units.

(b) Three replicates.

(c) Eight replicates; four on day 1 using calibration standards prepared with the 0.5, 1.0. amd 2.0 µg/ml set, and four on day 2 using calibration standards prepared with the 100, 250, and 500 µg/ml set.

TABLE 3. LINEAR REGRESSION ANALYSIS RESULTS OF LINEAR DYNAMIC RANGE ASSESSMENT OF THE GC-FID SYSTEM--EXTERNAL STANDARD METHOD

	Regression Analysis Parameter[a] for the Given Concentration Range					
	Full Concentration Range[b] (0.0 to 500 mg/L)			Low Concentration Range[b] (0.0 to 50 mg/L)		
Parameter	Slope	Intercept	Correlation Coefficient	Slope	Intercept	Correlation Coefficient
Acetonitrile	4.76	-9.2	0.9998	3.35	-0.37	0.99995
Acrolein	5.62	-15.6	0.9997	3.96	0.43	0.99999
Acrylonitrile	6.90	-15.1	0.9998	4.64	-0.75	0.99995

(a) Slope Units: Arbitrary GC peak area units per mg/L concentration
Intercept Units: Arbitrary GC peak area units

(b) All data from 2.0 μL injection. See Table 2 for the concentrations analyzed.

TABLE 4. GC PEAK AREA RATIOS(a) FOR DETERMINATION OF THE LINEAR DYNAMIC RANGE OF THE DETECTOR--INTERNAL STANDARD METHOD

		Average GC Peak Area Ratios(a) Obtained from 2 μL injections for the Given Concentration, mg/L								
Compound	Statistical Parameter	0.5(b)	1.0(b)	2.0(b)	4.0(c)	15.0(c)	50(c)	100(b)	250(b)	500(b)
Acetonitrile	Mean	0.034	0.066	0.161	0.321	1.24	4.07		20.4	39.4
	Standard Deviation	±0.004	±0.008	±0.004	±0.026	±0.23	±0.43	(d)	±1.3	±3.1
	Relative Standard Deviation, %	11.8	12	2.4	8.1	11	10.7		6.4	7.9
Acrolein	Mean	0.585	0.091	0.210	0.405	1.41	4.74		23.1	47.0
	Standard Deviation	±0.007	±0.007	±0.015	±0.025	±0.09	±0.41	(d)	±1.4	±3.3
	Relative Standard Deviation, %	12.3	7.7	7.4	6.2	6.9	8.8		6.2	7.2
Acrylonitrile	Mean	0.044	0.085	0.175	0.44	1.65	5.80		29.1	57.3
	Standard Deviation	±0.003	±0.018	±0.086	±0.036	±0.13	±0.54	(d)	±1.8	±4.2
	Relative Standard Deviation, %	7.7	21	49.2	8.1	8	9.4		6	7.4

(a) GC peak area of the designated analyte divided by that of the internal standard, 1-chloropropane, which was present in all samples at 15 μg/mL.

(b) 3 replicates.

(c) Eight replicates; four on day 1 using calibration standards prepared with the 0.5, 1.0, and 2.0 μg/mL set, and four on day 2 using calibration standards prepared with the 100, 250, and 500 μg/mL set.

(d) The internal standard level in this sample was incorrect, so that only external standard results are available (see Table 2).

TABLE 5. LINEAR REGRESSION ANALYSIS RESULTS OF LINEAR DYNAMIC RANGE ASSESSMENT OF THE GC-FID SYSTEM--INTERNAL STANDARD METHOD

	Regression Analysis Parameter[a] for the Given Concentration Range					
	Full Concentration Range[b] (0.0 to 500 mg/L)			Low Concentration Range[b] (0.0 to 50 mg/L)		
Parameter	Slope	Intercept	Correlation Coefficient	Slope	Intercept	Correlation Coefficient
Acetonitrile	0.079	0.059	0.99986	0.081	-0.017	0.9998
Acrolein	0.094	-0.006	0.99996	0.095	0.002	0.99994
Acrylonitrile	0.114	0.006	0.99997	0.112	-0.036	0.9998

(a) Slope Units: GC peak area ratio per mg/L concentration.
Intercept Units: GC peak area ratio units.

(b) All data from 2.0 μL injection. See Table 4 for the concentrations analyzed.

TABLE 6. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING METHOD 5030 WITH EXTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD(a)	MDL(b)	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.9	10.0	11.3	9.1	9.1	8.7	9.7	9.5	9.3	9.5	0.84	2.7	86
Acrolein	0.0	5.0	5.6	5.0	5.1	5.0	5.3	5.3	5.4	5.2	0.22	0.7	104
Acrylonitrile	1.1	5.0	5.6	5.2	5.2	5.2	5.3	5.3	5.2	5.3	0.15	0.5	84

(a) SD = Standard Deviation
(b) MDL = Method Detection Limit

TABLE 7. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING METHOD 5030 WITH INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								$SD^{(a)}$	$MDL^{(b)}$	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.9	10.0	11.7	9.4	9.2	9.2	10.2	9.7	9.5	9.8	0.89	2.8	89
Acrolein	0.0	5.0	5.6	5.0	5.0	5.2	5.4	5.4	5.5	5.3	0.24	0.7	106
Acrylonitrile	1.1	5.0	5.6	5.3	5.1	5.4	5.4	5.3	5.3	5.3	0.15	0.5	84

(a) SD = Standard Deviation
(b) MDL = Method Detection Limit

TABLE 8. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN GROUNDWATER USING EXTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD[a]	RSD,[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	10	10.7	10.0	10.3	9.7	9.7	9.5	9.1	9.9	0.5	5.3	95
Acrolein	0.1	5	4.6	4.6	4.7	4.5	4.6	4.5	4.4	4.6	0.1	2.1	90
Acrylonitrile	0.8[c]	10	10.2	10.0	10.2	9.9	10.3	10.5	10.0	10.2	0.2	2.0	94

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation
(c) Retention time of background material was incorrect but chromatographic separation was insufficient to resolve background material from acrylonitrile in the spiked samples.

TABLE 9. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN GROUNDWATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD(a)	RSD,(b) %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	10.0	10.6	10.2	10.4	9.7	10.0	9.6	8.9	9.9	0.6	5.8	95
Acrolein	0.1	5.0	4.6	4.7	4.7	4.5	4.6	4.6	4.3	4.6	0.1	3.0	90
Acrylonitrile	0.8(c)	10.0	10.2	10.2	10.3	9.9	10.5	10.6	9.7	10.2	0.3	3.0	94

(a) SD = Standard Deviation

(b) RSD, % = Percent Relative Standard Deviation

(c) Retention time of background material was incorrect but chromatographic separation was insufficient to resolve background material from acrylonitrile in the spiked samples.

TABLE 10. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN GROUNDWATER USING EXTERNAL STANDARD CALIBRATION

Compound	Background Level, μg/L	Amount Spiked, μg/L	Amount Found in Given Replicate, μg/L								SD[a]	RSD,[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	2.0	150	143	143	150	135	144	122	133	139	9	6.5	91
Acrolein	0.0	75	72	72	74	72	72	68	69	71	2	3.1	95
Acrylonitrile	2.0 (c)	75	67	66	67	66	67	63	64	66	1	2.1	85

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation
(c) Retention time of background material was incorrect but chromatographic separation was insufficient to resolve background material from acrylonitrile in the spiked samples.

TABLE 11. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN GROUNDWATER USING INTERNAL STANDARD CALIBRATION

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Replicate, µg/L								SD[a]	RSD,[b] %	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.7	150	139	144	153	136	147	128	141	141	8	5.7	93
Acrolein	0.2	75	70	73	75	72	73	71	73	72	2	2.5	96
Acrylonitrile	2.0[c]	75	65	67	68	66	68	66	68	67	1	1.9	87

(a) SD = Standard Deviation

(b) RSD, % = Percent Relative Standard Deviation

(c) Retention time of background material was incorrect but chromatographic separation was insufficient to resolve background material from acrylonitrile in the spiked samples.

TABLE 12. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POLYETHYLENE GLYCOL USING METHOD 5030 WITH EXTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg											
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD(a)	RSD, %(b)	MDL(c)	Average Percent Recovery
Acetonitrile	0.3	3.0	4.0	3.4	3.0	3.4	3.1	3.2	3.2	3.3	0.3	10	1.0	100
Acrolein	0.7	1.0	2.0	2.0	1.6	1.8	1.5	1.6	1.6	1.7	0.2	12	0.7	100
Acrylonitrile	0.0	1.0	1.1	1.1	1.1	1.1	1.0	1.0	1.0	1.00	0.05	5.3	0.2	100

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) MDL = Method Detection Limit, mg/kg, assuming a 2.0 g sample weight extracted with 40 mL PEG and a 200 µL PEG aliquot analyzed.

TABLE 13. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN POLYETHYLENE GLYCOL USING METHOD 5030 WITH INTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg											
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD[a]	RSD, %[b]	MDL[c]	Average Percent Recovery
Acetonitrile	0.3	3.0	4.1	3.3	2.9	3.4	3.0	3.2	3.2	3.3	0.4	13	1.2	100
Acrolein	0.7	1.0	2.0	2.0	1.6	1.7	1.5	1.6	1.6	1.7	0.2	12	0.6	100
Acrylonitrile	0.0	1.0	1.2	1.1	1.0	1.1	1.0	1.0	1.0	1.0	0.08	7.9	0.3	100

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) MDL = Method Detection Limit, mg/kg, assuming a 2.0 g sample weight extracted with 40 mL PEG and a 200 uL PEG aliquot analyzed.

TABLE 14. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5030 AND PEG EXTRACTION WITH EXTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.0	15	16.1	15.0	14.5	17.6	17.2	13.6	17.0	15.8	1.5	9.6	99
Acrolein	0.1	5	0.6	0.5	0.6	0.6	0.6	0.6	0.5	0.6	0.05	8.1	10
Acrylonitrile	0.3	5	4.2	4.0	4.0	4.4	4.1	3.8	4.2	4.1	0.2	4.7	76

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 15. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5030 AND PEG EXTRACTION WITH INTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD[(a)]	RSD, %[(b)]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.0	15	14.8	15.4	14.8	17.7	17.0	13.3	16.4	15.6	1.5	9.7	97
Acrolein	0.1	5	0.5	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.05	8.1	10
Acrylonitrile	0.3	5	3.9	4.2	4.2	4.4	4.2	3.8	4.1	4.1	0.2	5.0	76

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 16. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5030 AND PEG EXTRACTION WITH EXTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD(a)	RSD, %(b)	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.2	100	88.2	112.7	113.9	82.8	92.8	91.1	101.3	97.5	12.1	12.4	96
Acrolein	0.2	50	4.5	4.8	4.7	4.1	4.5	4.0	4.3	4.4	0.3	6.7	8
Acrylonitrile	0.3	100	84.2	89.7	88.5	81.4	86.7	78.3	79.3	84.0	4.5	5.4	84

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 17. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5030 AND PEG EXTRACTION WITH INTERNAL STANDARD CALIBRATION

Compound	Background Level, mg/kg	Amount Spiked mg/kg	Amount Found in Given Replicate, mg/kg								SD[a]	RSD %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	1.2	100	85	108	111	80	90	87	98	94	12	13	93
Acrolein	0.2	50	4.4	4.6	4.6	4.0	4.4	3.9	4.2	4.3	0.3	6.4	8
Acrylonitrile	0.2	100	81	86	86	79	84	75	77	81	5	5.6	81

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 18. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN TOLUENE USING DIRECT INJECTION

Compound	Amount Spiked, mg/L	Amount Found in Given Replicate, mg/L								SD$^{(a)}$	RSD, %$^{(b)}$	MDL$^{(c)}$	Average Percent Recovery
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average				
Acetonitrile	3.0	3.0	3.5	3.3	2.9	3.0	3.4	3.4	3.2	0.2	7.5	0.8	107
Acrolein	3.0	2.9	3.0	2.8	3.2	2.7	3.0	2.7	2.9	0.2	6.3	0.6	97
Acrylonitrile	3.0	3.4	3.1	3.0	2.9	3.1	3.1	3.3	3.1	0.2	5.5	0.5	103

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) MDL = Method detection limit calculations based upon the assumption that 5 µL of neat organic liquid waste is injected.

TABLE 19. RESULTS OF BACKGROUND LEVEL DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING METHOD 8030 AND DIRECT INJECTION

Compound	Amount Spiked, mg/L	Amount Found in Given Replicate, ng/μL									
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD[(a)]	RSD, %[(b)]
Acetonitrile	0.0	0.38	0.40	0.40	0.53	0.43	0.36	0.45	0.42	0.06	13
Acrolein	0.0	0.21	0.08	0.00	0.08	0.07	0.18	0.02	0.09	0.08	86
Acrylonitrile	0.0	3.34	3.19	3.18	2.86	3.00	3.17	2.87	3.09	0.18	6

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 20. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING DIRECT INJECTION

Compound	Background Level, mg/L	Amount Spiked, mg/L	Amount Found in Given Replicate, mg/L								SD(a)	RSD, %(b)	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	2.5	2.64	2.50	2.57	2.52	2.58	2.60	2.55	2.56	0.05	1.8	86
Acrolein	0.1	2.5	2.48	2.46	2.60	2.47	2.36	2.38	2.45	2.46	0.08	3.1	94
Acrylonitrile	3.1	12.5	17.1	17.1	17.7	17.2	16.9	16.9	16.4	17.0	0.4	2.3	111

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 21. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING DIRECT INJECTION

Compound	Background Level, mg/L	Amount Spiked, mg/L	Amount Found in Given Replicate, mg/L								SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	124	133	132	138	163	137	142	112	137	15	11	109
Acrolein	0.1	124	134	120	121	153	123	128	104	126	15	12	101
Acrylonitrile	3.1	124	132	121	121	152	124	128	102	126	15	12	98

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.

TABLE 22. RESULTS OF METHOD 8030 DETECTION LIMIT DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN REAGENT WATER USING METHOD 5020

Compound	Spike Level, mg/L	Amount Found in Given Replicate, mg/L											
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD[a]	RSD, %[b]	MDL[c]	Average Percent Recovery
Acetonitrile	1.0	0.58	1.80	1.21	0.87	0.79	1.29	0.90	1.1	0.4	33	1	110
Acrolein	1.0	0.60	0.67	0.48	0.71	0.52	0.60	0.76	0.6	0.1	16	0.3	60
Acrylonitrile	1.0	0.54	0.69	0.55	0.76	0.47	0.44	0.57	0.6	0.1	20	0.4	60

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) MDL = Method Detection Limit, mg/L.

TABLE 23. RESULTS OF BACKGROUND LEVEL DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHODS 5020 AND 8030

Compound	Spike Level, mg/kg	Amount Found in Given Replicate, mg/kg									
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD[a]	RSD, %[b]
Acetonitrile	0	0.50	0.39	0.21	1.4	3.2[d]	0.40	0.56	0.6	0.4	70
Acrolein	0	--[c]	--	--	--	--	--	--	--	--	--
Acrylonitrile	0	13	14	3.5	26	86.4[d]	5.6	4.1	11	8	80

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) Dash (--) indicates compound was not detected.
(d) Rejected using Q-test (4) at 90% confidence level.

TABLE 24. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALDIATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5020

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD[a]	RSD, %[b]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.6	10	6.7	3.9	5.6	7.5	4.8	0.5	7.5	5.2	2.5	48	46
Acrolein	ND[c]	20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	11	100	44	28	46	49	47	5.8	76	42	22	51	32

(a) SD = Standard Deviation
(b) RSD, % = Percent Relative Standard Deviation
(c) ND = Acrolein not determined due to decomposition in standards and spiked samples during the 1 hour equilibration at 90°C.

TABLE 25. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN SOLID WASTE USING METHOD 5020

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD(a)	RSD, %(b)	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.6	100	91	102	260	83	44	70	209	120	80	65	120
Acrolein	ND(c)	100	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	11	500	470	390	3400(d)	380	270	420	1730(d)	390	80	20	76

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) ND = Acrolein not determined due to decomposition in standards and spiked samples during the 1 hour equilibration at 90°C.
(d) These values rejected using successive application of the Q-test (4) at the 90% confidence level and are not included in the average.

TABLE 26. RESULTS OF BACKGROUND LEVEL DETERMINATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING METHODS 5020 AND 8030

Compound	Spike Level, mg/kg	Amount Found in Given Replicate, mg/kg								SD[(a)]	RSD, %[(b)]
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average		
Acetonitrile	0.0	0.65	0.84	0.58	0.27	0.35	0.09	0.0	0.4	0.3	75
Acrolein	0.0	ND(c)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	0.0	4.8	13.6	7.6	6.4	4.1	39.2(d)	4.1	7	4	60

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation
(c) ND = Acrolein not determined due to decomposition in standards and spiked samples during the 1 hour equilibration at 90°C.
(d) This value rejected with the Q-test (4) at the 99% confidence level.

TABLE 27. RESULTS OF METHOD 8030 LOW SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING METHOD 5020

Compound	Background Level, mg/kq	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD[(a)]	RSD, %[(b)]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	10	29	-45	38	3.2	9.8	-21	-25	-2	30	1900	-20
Acrolein	ND[(c)]	10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	7	50	61	-260	68	12.3	43	1680	-1310	40	890	2100	70

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) ND = Acrolein not determined due to decomposition in standards and spiked samples during the 1 hour equilibration at 90°C.

TABLE 28. RESULTS OF METHOD 8030 HIGH SPIKE LEVEL VALIDATION FOR ACETONITRILE, ACROLEIN. AND ACRYLONITRILE IN ORGANIC LIQUID WASTE USING METHOD 5020

Compound	Background Level, mg/kg	Amount Spiked, mg/kg	Amount Found in Given Replicate, mg/kg								SD[(a)]	RSD, %[(b)]	Average Percent Recovery
			Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Acetonitrile	0.4	100	1140	68	31	671	430	320	2400	700	800	110	700
Acrolein	ND[(c)]	100	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	7.0	500	1410	204	141	1960	1320	-510	4200	1200	1600	1300	250

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) ND = Acrolein not determined due to decomposition in standards and spiked samples during the 1 hour equilibration at 90°C.

TABLE 29. SUMMARY OF METHOD VALIDATION RESULTS

Method(a) (Matrix)	Acetonitrile			Acrolein			Acrylonitrile		
		Percent Recovery + Percent RSD(c)			Percent Recovery + Percent RSD(c)			Percent Recovery + Percent RSD(c)	
	MDL(b)	Low Spike	High Spike	MDL(b)	Low Spike	High Spike	MDL(b)	Low Spike	High Spike
5030, HP&T (groundwater)	3 μg/L	95 ± 5	92 ± 6	0.7 μg/L	90 ± 2	95 ± 6	0.5 μg/L	94 ± 2	86 ± 2
5030, PEG/HP&T (solid waste)	1 mg/kg(d)	98 ± 10	95 ± 13	0.7 mg/kg(d)	10 ± 8	8 ± 7	0.3 mg/kg(d)	76 ± 5	83 ± 6
DLI (liquid waste)	0.8 mg/L	86 ± 2	109 ± 11	0.6 mg/L	94 ± 3	101 ± 12	0.5 mg/L	111 ± 2	98 ± 12
5020, HHS	1 mg/kg			0.3 mg/kg			0.4 mg/kg		
(solid waste)		46 ± 48	120 ± 65		(e)	(e)		32 ± 51	76 ± 20
(liquid waste)		-20 ± 1900	700 ± 100		(e)	(e)		70 ± 2100	250 ± 1300

(a) HP&T: heated purge-and-trap; PEG: polyethylene glycol; DLI: direct liquid injection; HHS: heated headspace sampling.

(b) Matrices: HP&T, buffered reagent water and groundwater; PEG/HP&T, reagent PEG; DLI, toluene; HHS, buffered reagent water.

(c) RSD = Relative Standard Deviation.

(d) Assuming a 1-gm sample extracted with 40 mL PEG and a 200-μL PEG extract aliquot analyzed.

(e) Acrolein was not stable under HHS conditions.

SECTION 6

QUALITY ASSURANCE

Quality assurance measures in effect throughout the program included the following:

- Fresh stock solutions were prepared from neat acrolein on a daily basis due to the instability of this compound.
- Fresh calibration standards for quantification purposes were prepared on a daily basis.
- For all Method 5030 work, a system blank consisting of a dry run of the purge-and-trap system and gas chromatograph was the first instrument run of the day. This blank run checked for contamination of the purge-and-trap system and proper operation of the equipment. A reagent water blank was run as the second run each day to check on the purity of the water used to prepare the purge-and-trap calibration standards.
- Except for Method 5020 (see below), each day that method validation data were generated the instrument response was calibrated with a minimum of three levels of calibration standards which encompassed the concentration range anticipated for samples to be analyzed.
- For all Method 5030 work, an internal standard was included in each purge-and-trap GC run to monitor the retention times and as a check on the transfer efficiency of sample from purge-and-trap to the GC.

Method 5020, heated headspace sampling, employs a standard addition quantification approach (see Section 4) which does not involve the analysis of separate calibration standards and the subsequent generation of calibration response factors for each analyte. The only QA check specified by the method is to ensure that the instrument response is "on scale" which, for this work, involved verification that FID outputs did not exceed the analog-to-digital converter of the GC data system.

For the remainder of the validation work, the DLI data sets and the Method 5030 data sets were quantified by the external standard/average response factor method. In addition, all of the Method 5030 data was also quantified by the internal standard/average response factor method. Summaries of and relevant statistics for the external standard method average response factors for any given days work for purge-and-trap analysis of groundwater, PEG/purge-and-trap analysis of solid waste, and DLI analysis of liquid waste are presented in Tables 30, 31, and 32, respectively. The corresponding internal standard method response factors for groundwater and solid waste are presented in Tables 33, and 34, respectively. Tables 30 through 34 represent all of the response factors used to calculate the seven replicate validation recoveries reported. Only six of the 42 relative standard deviation values in Tables 30 through 34 are greater than 10 percent, an no RSD values exceed 13 percent for response factors.

TABLE 30. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE FOR GROUNDWATER ANALYSIS BY METHODS 8030 AND 5030

Compound	Date of Analysis	Calibration Range, µg/L	Response Factor Parameter			
			N(a)	Average	SD(b)	RSD, %(c)
Acetonitrile	3/15/84	20-200	4	3.14	0.19	5.9
Acetonitrile	3/16/84	6-60	4	3.15	0.41	13
Acrolein	3/15/84	10-100	4	1.94	0.09	4.5
Acrolein	3/16/84	3-30	4	2.08	0.17	8.1
Acrylonitrile	3/15/84	10-100	4	1.15	0.05	4.6
Acrylonitrile	3/16/84	3-30	4	1.18	0.09	8.3

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation.

TABLE 31. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE FOR ANALYSIS OF PEG SOLID WASTE EXTRACTS BY METHODS 8030 AND 5030

Compound	Date of Analysis	Calibration Range, mg/kg(a)	Response Factor Parameter			
			N(b)	Average	SD(c)	RSD, %(d)
Acetonitrile	4/11/84	20-200	3	1.81	0.03	1.8
Acetonitrile	4/12/84	2-20	3	2.45(e)	0.16	6.4
Acetonitrile	4/18/84	2-20	5	1.85	0.20	11
Acrolein	4/11/84	10-100	3	0.95	0.06	5.9
Acrolein	4/12/84	1-10	3	1.06	0.07	6.4
Acrolein	4/18/84	1-10	5	0.90	0.08	8.4
Acrylonitrile	4/11/84	10-100	3	0.67	0.03	4.0
Acrylonitrile	4/12/84	1-10	3	0.72	0.02	2.3
Acrylonitrile	4/18/84	1-10	5	0.71	0.02	2.7

(a) Assuming a 2.0 gm sample extracted with 40 mL of PEG and a 200 μL PEG extract analyzed.

(b) Number of calibration standards analyzed on the given day.

(c) SD = Standard Deviation.

(d) RSD, % = Percent Relative Standard Deviation.

(e) Due to the significant difference from historical response factors, this value was rejected. Instead, a response factor (1.89) which was the average of those for 4/11/84 and 4/12/84 was used.

TABLE 32. EXTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE~~, ACROLEIN, AND ACRYLONITRILE~~ FOR THE ANALYSIS OF LIQUID ORGANIC WASTE BY DIRECT INJECTION

Compound	Date of Analysis	Calibration Range, mg/L	Response Factor Parameter			
			N(a)	Average	SD(b)	RSD, %(c)
Acetonitrile	4/18/84	2-20	6	4.95	0.37	7.6
Acetonitrile	4/23/84	2-20	3	1.30	0.09	7.2
Acetonitrile	4/24/84	20-200	8	1.73	0.02	1.2
Acetonitrile	4/29/84	2-20	7	0.844	0.017	2.0
Acrolein	4/18/84	2-20	6	4.82	0.41	8.6
Acrolein	4/23/84	2-20	3	1.45	0.20	14
Acrolein	4/24/84	20-200	8	1.66	0.12	7.2
Acrolein	4/29/84	2-20	7	0.97	0.08	8.3
Acrylonitrile	4/18/84	2-20	6	3.03	0.30	9.9
Acrylonitrile	4/23/84	2-20	3	1.21	0.15	13
Acrylonitrile	4/24/84	20-200	8	1.29	0.06	4.9
Acrylonitrile	4/29/84	2-20	7	0.73	0.02	3.3

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation.

TABLE 33. INTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE FOR GROUNDWATER ANALYSIS BY METHODS 8030 AND 5030

Compound	Date of Analysis	Calibration Range, µg/L	Response Factor Parameter N(a)	Average	SD(b)	RSD, %(c)
Acetonitrile	3/15/84	20-200	4	2.35	0.15	6.3
Acetonitrile	3/16/84	6-60	4	2.4	0.3	12
Acrolein	3/15/84	10-100	4	1.45	0.06	4.1
Acrolein	3/16/84	3-30	4	1.60	0.12	7.8
Acrylonitrile	3/15/84	10-100	4	0.86	0.04	4.6
Acrylonitrile	3/16/84	3-30	4	0.91	0.07	7.2

(a) Number of calibration standards analyzed on the given day.
(b) SD = Standard Deviation.
(c) RSD, % = Percent Relative Standard Deviation.

TABLE 34. INTERNAL STANDARD CALIBRATION RESPONSE FACTORS FOR ACETONITRILE, ACROLEIN, AND ACRYLONITRILE FOR ANALYSIS OF PEG SOLID WASTE EXTRACTS BY METHODS 8030 AND 5030

Compound	Date of Analysis	Calibration Range, mg/kg[a]	Response Factor Parameter			
			N[b]	Average	SD[c]	RSD, %[d]
Acetonitrile	4/11/84	20-200	3	2.76	0.14	5.2
Acetonitrile	4/12/84	2-20	3	3.82[e]	0.18	4.6
Acetonitrile	4/18/84	2-20	5	2.6	0.3	11
Acrolein	4/11/84	10-100	3	1.45	0.08	5.5
Acrolein	4/12/84	1-10	3	1.66	0.07	4.3
Acrolein	4/18/84	1-10	5	1.26	0.11	8.7
Acrylonitrile	4/11/84	10-100	3	1.01	0.04	4.4
Acrylonitrile	4/12/84	1-10	3	1.116	0.004	0.3
Acrylonitrile	4/18/84	1-10	5	1.00	0.03	2.9

(a) Assuming a 2.0 gm sample extracted with 40 mL of PEG and a 200 μL PEG extract analyzed.

(b) Number of calibration standards analyzed on the given day.

(c) SD = Standard Deviation

(d) RSD, % = Percent Relative Standard Deviation.

(e) Due to the significant difference from historical response factors, this value was rejected. Instead, a response factor (2.91) which was the average of those for 4/11/84 and 4/12/84 was used.

REFERENCES

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3. Evaluation of Office of Solid Waste Methods 8030 and 8090. Report for U.S. Environmental Protection Agency Contract No. 68-03-1760, Work Assignment 3, May 2, 1984.

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APPENDIX A

METHOD 8030

ACROLEIN, ACRYLONITRILE, ACETONITRILE

1.0 Scope and Application

1.1 Method 8030 is used to determine the concentration of three volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8030 is used to detect the following substances:

Acrolein (Propenal)
Acrylonitrile
Acetonitrile

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

2.1 Method 8030 provides chromatographic conditions for the detection of certain halogenated volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC column: 6-ft x 1/8-in. stainless steel or 6-ft x 1/4-in. glass column packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.6 Detector: Flame ionization (FID).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100 µl.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5-ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds being analyzed, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.1 Place about 8 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100-µl syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the alcohol without contacting the neck of the flask.

5.3.3 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.4 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C and for the 2-chloroethylvinyl ether. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µl of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25-µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 For standards prepared in 500- or 1,000-ml flasks, discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr unless stored and sealed as stipulated in Sections 6.1 and 6.3.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 min.

6.4 All samples must be analyzed within 14 days of collection.

7.0 Procedures

7.1 The recommended gas chromatographic column and operating conditions for the instrument are: Set helium gas flow at 45 ml/min flow rate. Set column temperature at 80° C for 5 min, then program an 8° C/min temperature rise to 150° C and until all compounds elute.

7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.2.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Because of these limitations, no internal standard that would be applicable to all samples can be suggested. The compounds recommended for use as surrogate spikes have been used successfully as internal standards, because of their generally unique retention times.

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured

A_{is} = Response for the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Method detection limit[a] (µg/l)
Acrolein	8.2	0.6
Acrylonitrile	9.8	0.5

[a] Method detection limit is based upon recovery of 5.0 µg/l dose into tap water.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Acrolein	96	11.6	20	7	1
Acrylonitrile	107	5.6	20	7	1

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.

2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.

3. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).

4. Going, John, et al. 1979. Environmental monitoring near industrial sites - Acrylonitrile. EPA Report No. 560/6-79-003.

APPENDIX B

METHOD 5020

HEADSPACE METHOD

1.0 Scope and Application

1.1 Method 5020 is a static headspace technique for extracting volatile organic compounds in pastes, solids, and liquids. It is a simple method that allows large numbers of samples to be analyzed in a relatively short period of time. Because of the large variability and complicated matrices of waste samples in the solid and paste forms, detection limits for this method may vary widely among samples. The method works best for compounds with boiling points of less than 125° C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

The sample is collected in sealed glass containers and allowed to equilibrate at 90° C. A sample of the headspace gas is withdrawn with a gas-tight syringe for analysis by the appropriate gas chromatographic method (8010, 8015, 8020, or 8030).

3.0 Interferences

Refer to Methods 8010, 8015, 8020, or 8030.

4.0 Apparatus and Materials

4.1 Gas-tight syringe: 5-cc with chromatographic needles.

4.2 Headspace standard solutions: Prepare according to procedures in 8010, 8015, 8020, or 8030 at 50 ng/µl and 250 ng/µl concentrations.

4.3 Vials: 125-ml Hypo-Vials (Pierce Chemical Co., #12995, or equivalent).

4.4 Septa: Tuf-Bond (Pierce #12720, or equivalent).

4.5 Seals: Aluminum (Pierce #13214, or equivalent).

4.6 Crimper: Hand (Pierce #13212, or equivalent).

5.0 Reagents

5.1 Refer to Methods 8010, 8015, 8020, or 8030.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Methods 8010, 8015, 8020, or 8030.

7.0 Procedure

7.1 Place 10.0 g each of the well-mixed waste sample into three separate 125-ml septum seal vials.

7.2 Dose one sample vial through the septum with 200 µl of a 50-ng/µl methanolic standard of the compounds of interest. Label this "1-ppm spike."

7.3 Dose a separate (empty) 125-ml septum seal vial with 200 µl of the 50 ng/µl standard methanol solution. Label this "1-ppm standard."

7.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90° C water bath for 1 hr. Store the remaining sample vial at 4.0° C for possible future analysis.

7.5 While maintaining the vials at 90° C, withdraw 2 ml of the headspace gas with a gas-tight syringe and analyze by injecting into a GC, operating under the appropriate conditions for the GC measurement method being used (8010, 8015, 8020, or 8030).

7.6 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2x the background. Record retention times (RT) and peak areas of compounds of interest.

7.7 Analyze the 1-ppm spiked sample in the same manner. Record RT's and peak areas.

7.8 Analyze the undosed sample as in Section 7.7.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

9.0 References

1. Hachenberg, H. and Schmidt, A. 1979. Gas chromatographic headspace analysis. Philadelphia: Hayden & Sons Inc.

2. Friant, S.L. and Suffet, I.H. 1979. Interactive effects of temperature, salt concentration, and pH on headspace analysis for isolating volatile trace organics in aqueous environmental samples. Anal. Chem. 51:2167-2172.

APPENDIX C

METHOD 5030

PURGE-AND-TRAP METHOD

1.0 Scope and Application

1.1 Method 5030 is used to determine the concentration of volatile organic compounds in a variety of liquid and solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, groundwater, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method also depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

1.4 Method 5030 is based upon a purge-and-trap, gas chromatographic procedure.

1.5 This method is recommended for use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs and skilled in the interpretation of chromatograms.

2.0 Summary of Method

2.1 A portion of solid waste is dispersed in polyethylene glycol (PEG) or distilled-in-glass methanol to dissolve the volatile organic constituents. A portion of the PEG or methanol solution is combined with water in a specially designed purging chamber. For liquid and some semiliquid samples, PEG or methanolic extraction will not be necessary. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. (SPECIAL NOTE: For Methods 8020 and 8030, drying of the trap for 4 min under helium flow is required. See Figure 5 for configuration.) The gas chromatographic column is heated to elute the components which are detected by the appropriate detector (Methods 8010, 8020, 8030).

3.0 Interferences

3.1 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.3.

3.2 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.4 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water (PEG or methanol solution) to check for cross contamination. After each use, the purging chamber is cleaned as described in Section 7.12. The trap and other parts of the system are also subject to contamination; therefore, frequent additional bakeout and purging or the entire system may be required.

4.0 Apparatus and Materials

4.1 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are commercially available.

4.1.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.1.2 The sorbent trap consists of a 1/8-in. O.D. (0.105-in. I.D.) x 25-cm-long stainless steel tube packed with the appropriate absorbents as described in Table 1 (see Figures 2 and 3).

4.1.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec.

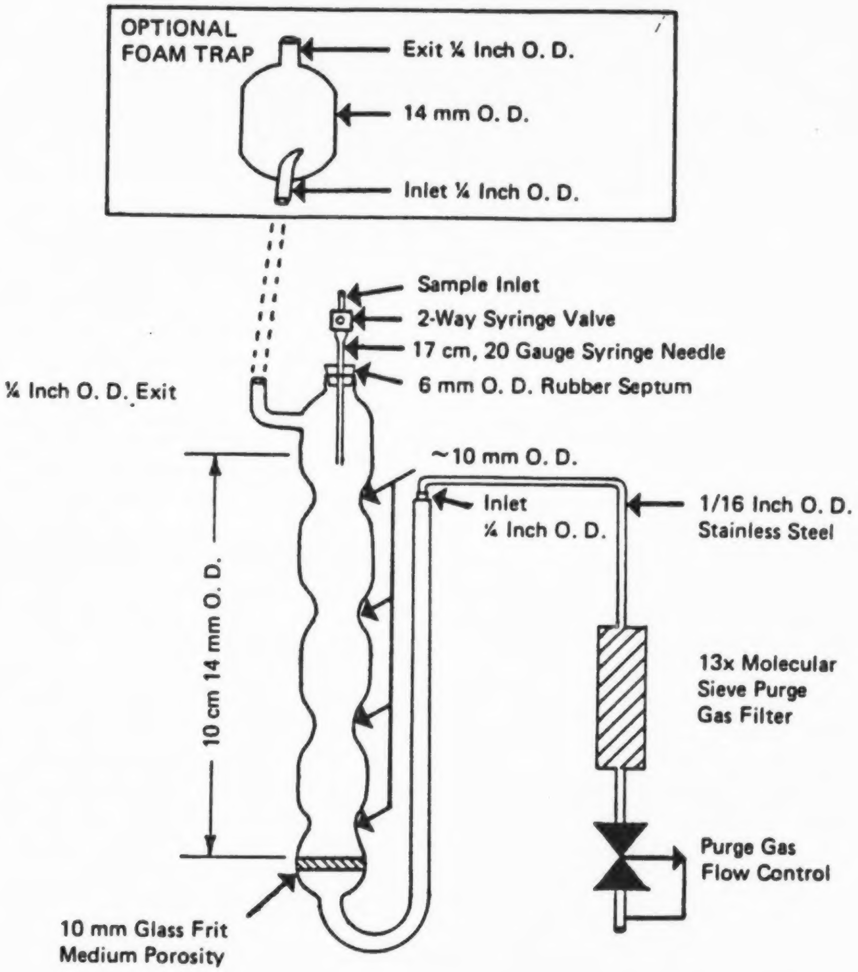


Figure 1. Purging chamber.

TABLE 1. PURGE-AND-TRAP PARAMETERS

	Analysis method[a]		
	8010	8020	8030
Purge Gas	Nitrogen or Helium	Nitrogen or Helium	Helium
Purge Gas Flow Rate (ml/min)	40	40	20 ± 1
Purge Time (min)	11.0	12.0	30.0
Purge Temperature	Ambient	Ambient	85° C
Desorb Temperature (°C)	180°	180°	100°
Sorbents to be used in packing tube	A	B	B

[a] Measurement method to be employed for identification and quantification.

KEY: A = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

Silica gel, 35/60 mesh Davison grade-15 or equivalent.

Coconut charcoal, 6/10 mesh, Barnaby Chaney C.A. - 580-26 lot #M-2649 or equivalent.

Refer to Figure 2 for column packing.

B = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

Refer to Figure 3 for column packing.

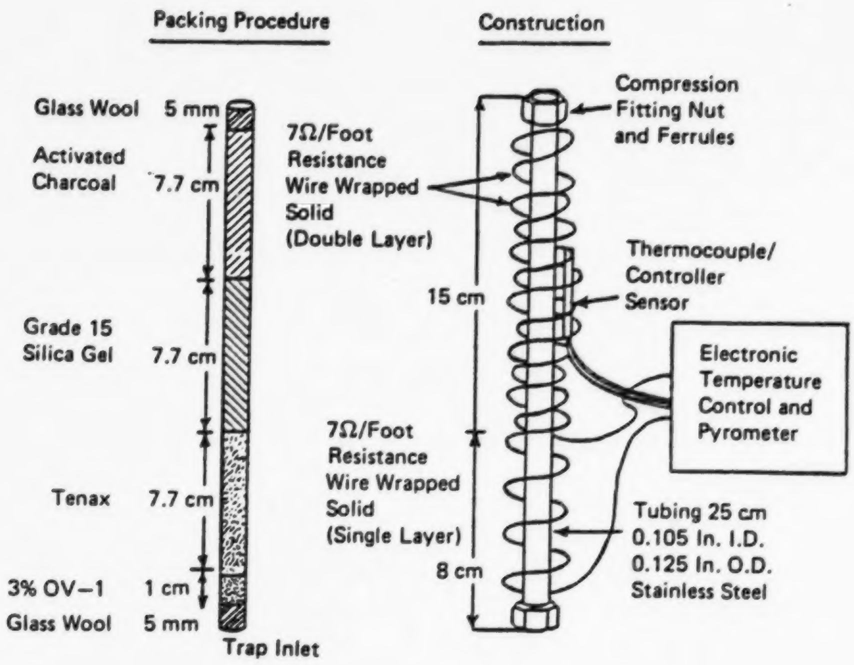

Packing Procedure
Construction
Glass Wool 5 mm
Activated Charcoal 7.7 cm
Grade 15 Silica Gel 7.7 cm
Tenax 7.7 cm
3% OV–1 1 cm
Glass Wool 5 mm
Trap Inlet
7Ω/Foot Resistance Wire Wrapped Solid (Double Layer)
7Ω/Foot Resistance Wire Wrapped Solid (Single Layer)
15 cm
8 cm
Compression Fitting Nut and Ferrules
Thermocouple/ Controller Sensor
Electronic Temperature Control and Pyrometer
Tubing 25 cm 0.105 In. I.D. 0.125 In. O.D. Stainless Steel

Figure 2. Trap packings and construction for Method 8010.

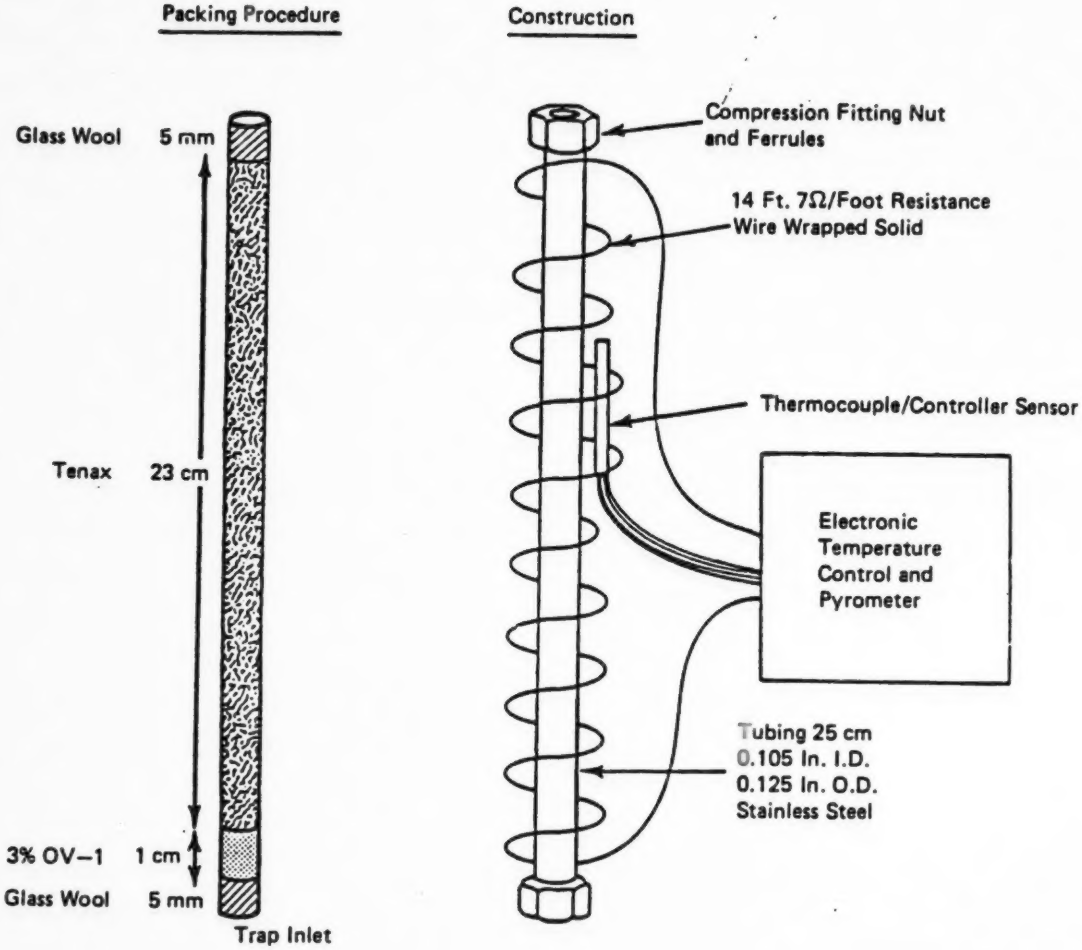

Packing Procedure
Construction
Glass Wool
5 mm
Tenax
23 cm
3% OV–1
1 cm
Glass Wool
5 mm
Trap Inlet
Compression Fitting Nut and Ferrules
14 Ft. 7Ω/Foot Resistance Wire Wrapped Solid
Thermocouple/Controller Sensor
Electronic Temperature Control and Pyrometer
Tubing 25 cm
0.105 In. I.D.
0.125 In. O.D.
Stainless Steel

Figure 3. Trap packing and construction for Methods 8020 and 8030.

4.1.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 4 through 6.

4.2 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.3 Micro syringes: 10 µl, 25 µl, 100 µl, 250 µl, 500 µl, and 1,000 µl. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.4 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation (Kimble #45212 or equivalent).

4.5 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.6 Syringe valve: 2-way, with Luer ends (2 each; Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting or equivalent).

4.7 Syringe: 5-ml, gas-tight with shutoff valve.

4.8 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.9 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.10 Rotary evaporator: Equipped with Teflon-coated seals (Buchi Rotavapor R-110 or equivalent).

4.11 Vacuum pump: Mechanical, two-stage.

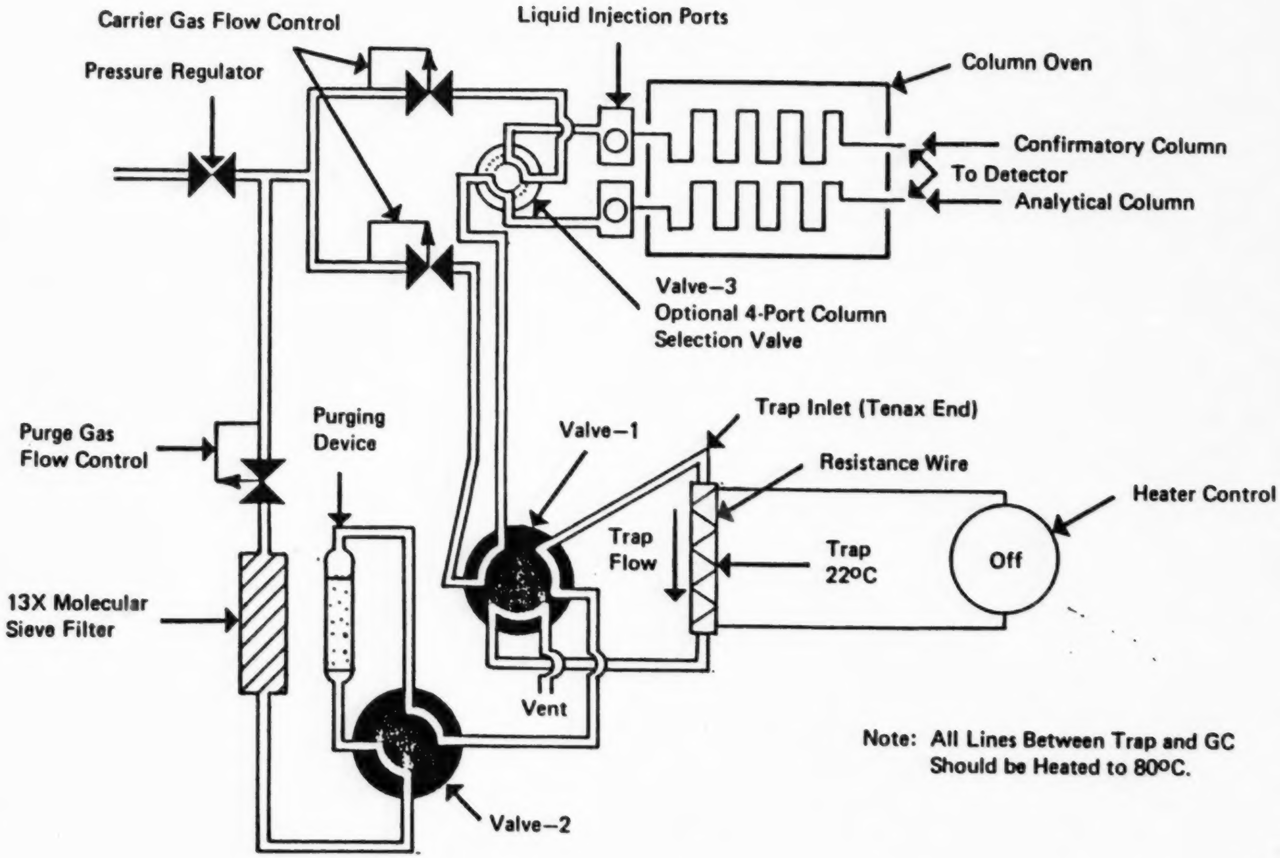
5.0 Reagents

5.1 Trap materials (see Table 1 and Figures 2 and 3 for configuration).

5.1.1 2,6-Diphenylene oxide polymer: 60/80 mesh Tenax, chromatographic grade or equivalent.

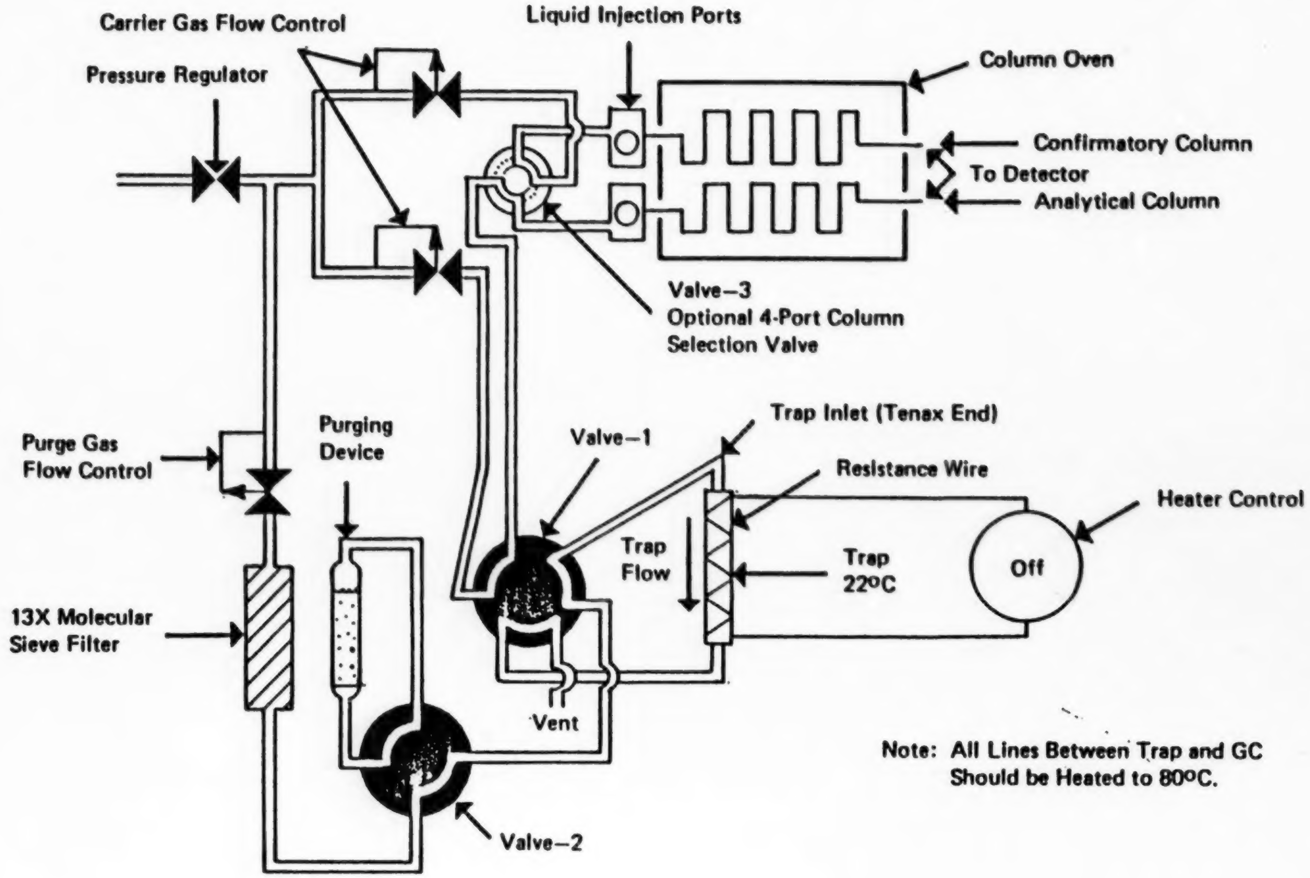
5.1.2 Methyl silicone packing: 3% OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.1.3 Silica gel, Davison Chemical (35/60 mesh), grade 15 or equivalent.



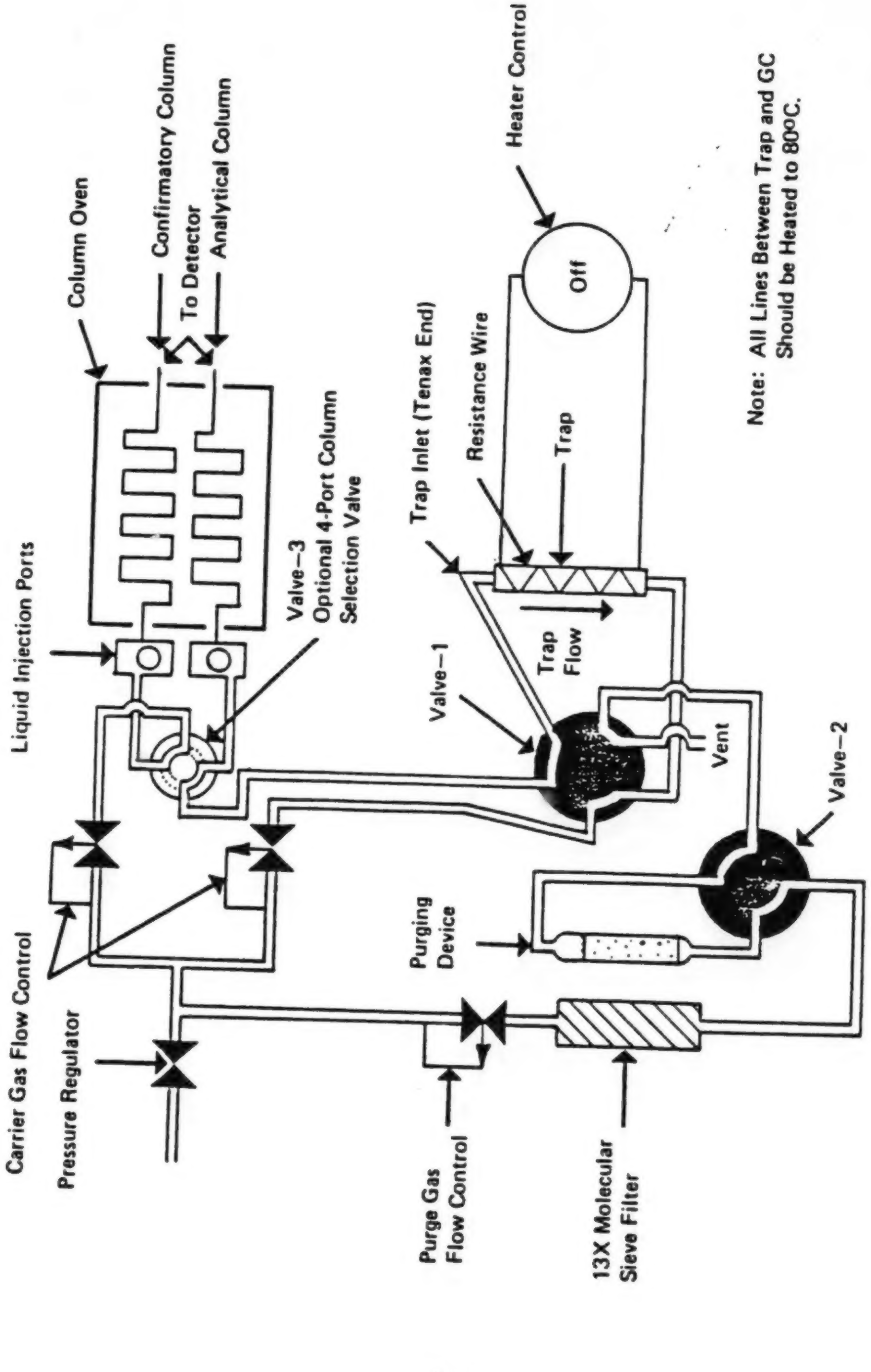
Note: All Lines Between Trap and GC Should be Heated to 80°C.

Figure 4. Purge-and-trap system, purge-sorb mode, for methods 8010, 8020 and 8030.



Note: All Lines Between Trap and GC
Should be Heated to 80°C.

Figure 5. Purge-and-trap system, trap dry mode, for Methods 8020 and 8030.



Note: All Lines Between Trap and GC
Should be Heated to 80°C.

Figure 6. Purge-and-trap system, desorb mode, for Methods 8010, 8020 and 8030.

5.2 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.2.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.3 Reagent PEG (polyethylene glycol; for solid samples): Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest. Methanol which has been distilled in glass can be used as a substitute for PEG.

5.3.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.3.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Method 8010, 8020, or 8030 for pertinent information.

7.0 Procedures

7.1 Assemble the purge-and-trap device (see Figures 4 through 6). Purge parameters to be used depend on the compounds being analyzed for; see Table 1. Pack the trap as shown in Figure 2 or 3 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the trap for 10 min by backflushing at 180° C.

7.2 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20-25° C.

7.3 Adjust the purge gas (nitrogen or helium) flow rate according to Table 1.

7.4 Operate the gas chromatograph using the conditions described in the appropriate method, 8010, 8020, or 8030.

7.5 Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

7.6 Remove the plunger from a 5-ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. (NOTE: For pastes it may be necessary to dilute the sample by adding a nonvolatile solvent to the sample. In such cases diluting can be performed in the purging device.)

7.7 PEG extraction procedure for solids (methanol which has been distilled in glass can be used as a substitute for PEG). Sample aliquots for extraction should be transferred as quickly as possible to minimize loss of volatiles from the sample.

7.7.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent PEG. Weigh the capped centrifuge tube and PEG on an analytical balance.

7.7.2 Using an appropriate implement, transfer approximately 2 g of sample to the PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the PEG as quickly as possible. Take care not to touch the sample-transfer implement to the PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.7.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.7.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.7.5 Add an aliquot of the sample extract to 5 ml reagent water.

7.8 Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the liquid samples for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.

7.9 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber. Close both valves and purge the sample for the time specified in Table 1. If Method 8020 will be used for analysis of the sample, dry the trap by maintaining a flow rate of 40 ml/min dry purge for 4 min.

7.10 Attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to the backflush temperature indicated in Table 1, while backflushing the trap with an inert carrier gas at 20 to 60 ml/min for 4 min. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30° C (or subambient, if problems persist) instead of the initial program temperature of 45° or 50° C.

7.11 Return the purge trap device to the purge mode.

7.12 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105° C.

7.13 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.14 The analysis of blanks is most important in the purge-and-trap technique since the purging device and the trap can become contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water. Blanks should be sealed, stored at 4° C, and analyzed with each group of samples.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
3. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane. Report for EPA Contract 68-03-2635 (in preparation).
4. Ligon, W.V. and H. Grade. 1981. Poly(ethylene glycol) as a diluent for preparation of standards for volatile organics in water. Anal. Chem. 53:920-921.